EXCIPLEXES IN FLUORESCENCE QUENCHING OF AROMATIC HYDROCARBONS BY TERTIARY ALIPHATIC AMINES

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ABSTRACT

Strong quenching of the fluorescence of aromatic hydrocarbons by tertiary aliphatic amines has been observed in solution at room temperature. Accompanying the fluorescence quenching of aromatic hydrocarbons, an anomalous emission is observed. This new emission is very broad, structureless and red-shifted from the original hydrocarbon fluorescence.

Kinetic studies indicate that this anomalous emission is due to an exciplex formed by an aromatic hydrocarbon molecule in its lowest excited singlet state with an amine molecule. The fluorescence quenching of the aromatic hydrocarbons is due to the depopulation of excited hydrocarbon molecules by the formation of exciplexes, with subsequent de-excitation of exciplexes by either radiative or non-radiative processes.

Analysis of rate constants shows the electron-transfer nature of the exciplex. Through the study of the effects on the frequencies of exciplex emissions of substituents on the hydrocarbons, it is concluded that partial electron transfer from the amine molecule to the aromatic hydrocarbon molecule in its lowest excited singlet state occurs in the formation of exciplex. Solvent effects on the exciplex emission frequencies further demonstrate the polar

nature of the exciplex.

A model based on this electron-transfer nature of exciplex is proposed and proves satisfactory in interpreting the exciplex emission phenomenon in the fluorescence quenching of aromatic hydrocarbons by tertiary aliphatic amines.

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INTRODUCTION

When two unsaturated molecules lie close to one another, the interaction between the π-electron distributions on the two molecules may be strong enough to modify the energies and the ordering of the electronic states. Interaction leading to binding is well known for both ground and excited states. "Molecular complexes", usually called charge transfer complexes, are bound in their ground states. Excited state complexes are typified by the pyrene excimer.

A detailed knowledge of these two phenomena is of increasing importance not only from the theoretical point of view in interpreting the origin of the stability and the physical properties of these molecular complexes, but also for a better understanding of the mechanisms of reactions that may go by way of charge-transfer intermediates (1).

Complexes formed by interaction of two ground state molecules can be investigated by various techniques because of their long lifetimes (2). Properties of the complexes and theory of their structures have been thoroughly reviewed (3).

To photochemists, the electronically excited molecular complexes are more important, since they may be intermediates in photochemical reactions. For instance, the photodimerizations of anthracene (4, 5) and β-methoxynaphtha-

lene (6, 7) have been suggested to involve excimer intermediates. Unfortunately, due to their short lifetimes, only limited number of techniques can be used in the investigation of excited complexes. Nevertheless, since the original observation of the pyrene excimer emission (8, 9), a number of works have been directed toward better understanding of this phenomenon.

Forster and Kasper first observed that the singlet emission spectrum of pyrene solutions consists a normal vibrationally structured band and a broad, structureless band which is red-shifted from the normal (8, 9). From a study of the concentration dependence of the absorption and emission spectra, it was concluded that this structureless emission band originated from a species formed by the association of a molecule in its lowest excited singlet state and one in the ground state. This species was named an excimer (10).

Since these original observations, it is found that the excimer fluorescence is not a property confined to pyrene and its derivatives. Many aromatic hydrocarbons exhibit the same behaviour in various phases (8-19). Furthermore, "mixed excimers" or "exciplexes" -- species formed from an excited aromatic hydrocarbon molecule and a ground state molecule of another aromatic hydrocarbon -- have been

observed (11, 14, 20).

These observations stimulated further work on elucidation of the rates of excimer and exciplex formation and decomposition reactions, their electronic decay processes, their electronic structure and the nature of the intermolecular force between the partners.

Kinetic methods have been widely employed in the interpretation of the mechanisms of the excimer formation and decomposition. The mechanistic scheme, as shown in equations 1-6, has been shown to be adequate to account for the variations of the fluorescence intensities and lifetimes of monomers and derived excimers as the concentrations of the fluorescent aromatic hydrocarbons are changed (9, 21, 22).

$H^* \xrightarrow{k_{fM}} H + h\nu_M$	Fluorescence of H^*	(1)
$H^* \xrightarrow{k_{iM}} H$	Non-radiative decay	(2)
$H^* + H \xrightarrow{k_{DM}} H_2^*$	Excimer formation	(3)
$H_2^* \xrightarrow{k_{fD}} H + H + h\nu_D$	Fluorescence of excimer	(4)
$H_2^* \xrightarrow{k_{iD}} H + H$	Non-radiative decay	(5)
$H_2^* \xrightarrow{k_{MD}} H^* + H$	Regeneration of H^* from dissociation of excimer	(6)

Here H represents the aromatic hydrocarbon molecule and an asterisk denotes a molecule in its lowest excited singlet state.

The rate of the pyrene excimer formation at room temperature has been found to be close to diffusion-controlled rate. However, for other excimers with relatively weak interactions between two partners, the formation rates are smaller than expected for diffusion-controlled processes (21, 22). This is also a reversible process, as shown in equation 6.

Comparison of the behaviour of some aromatic hydrocarbons with their substituted derivatives demonstrates that steric effects play an important role in the formation of excimers (25, 26). Large steric hindrance may inhibit the excimer formation.

Since the formation of the excimer is competitive with the radiative and non-radiative decay processes of the monomer excited state, excimers are most likely to be found from monomers having long lived fluorescence.

The relatively low quantum yields of excimer fluorescence in some systems in solution at room temperature are attributed to the high rates of the non-radiative decay processes of the excimer, including the possible chemical dimerization through excimer intermediates. When the magni-

tude of the interaction between the excited and ground state molecules is so strong that chemical combination occurs, the formation of a stable photo-dimer may completely eliminate the excimer fluorescence (23). This occurs with anthracene and many of its derivatives (5). The temperature dependence studies show that the excimer emission quantum yield is very sensitive to the temperature (24, 25).

The influences of the temperature and the solvent viscosity on excimer fluorescence have been reported (24, 25). The rate parameters, k_{iM}, k_{DM}, k_{iD} and k_{MD}, in the mechanistic scheme vary with the temperature according to the following relations, where R is universal gas constant:

$$k_{iM} = k^{\circ}_{iM} + k^{'}_{iM} \exp(-W_{iM}/RT),$$

$$k_{DM} = k^{'}_{DM} \exp(-W_{DM}/RT),$$

$$k_{iD} = k^{\circ}_{iD} + k^{'}_{iD} \exp(-W_{iD}/RT),$$

$$k_{MD} = k^{'}_{MD} \exp(-W_{MD}/RT).$$

The internal quenching parameters (k_{iM}, k_{iD}) are expressed in terms of temperature-independent components (k°_{iM}, k°_{iD}) and temperature-dependent components, described by frequency factors ($k^{'}_{iM}$, $k^{'}_{iD}$) and activation energies (W_{iM}, W_{iD}).

By investigating the ratio of the quantum yield for excimer emission to that of monomer emission over two

different temperature ranges, the activation energy for the formation of the excimer W_{DM} (from low temperature range) and its binding energy $B = W_{MD} - W_{DM}$ (from high temperature range) may be obtained (24-25).

From these studies, many properties of excimers can be directly measured. The enthalpies and entropies of this kind of photo-association have been reported (15). It is found that both the radiative transition probability, k_{fD}, and the binding energy of the excimer are independent of its environment (i.e., temperature and solvent). However, the solvent viscosity determines the rate of the excimer formation and the activation energy for the process (24).

All these works, in turn, stimulated theoretical speculation as to the exact nature of excimer emissions and the structures of the excited state interactions which are responsible for the stabilization of the excimer with respect to the monomer. Two theoretical lines have been considered.

Forster originally suggested that the red shift of the excimer emission relative to the monomer emission was the result of a large Davydov, or exciton splitting of the excited state of the monomer. This results from the close approach of an excited state molecule and a ground-state molecule (27). He proposed two requirements: (1) the low-

est state of the monomer must be an ^1L_b state with a nearby ^1L_a state; and (2) the ^1L_a state must be split in the excimer such that its lower component would lie below that of ^1L_b state component. The excimer fluorescence is attributed to the transitions from the lower ^1L_a component into the repulsive ground state.

However, the Forster conditions were later found not to be rigorously required. Some hydrocarbons whose lowest singlet excited state is ^1L_a have been shown to exhibit excimer fluorescence. The examples of this type of compounds are 9-methylanthracene and perylene (11). Furthermore, it has been shown that the energy level splittings arising from dipole-dipole interactions are too small to explain the experimental results unless unreasonably small intermolecular separations are assumed (28).

Alternatively, it was suggested that the excimer state is essentially a charge-transfer state, or more correctly, a charge resonance state when two molecules are identical. However, from many experimental results, it has been shown that charge-transfer interactions can only account for part of the stability of the excimer (14, 20, 28-31).

Eventually, these two original approaches were combined. That is, the electronic states of the excimer are constructed by using the configurational mixing of the neu-

tral locally excited states with charge-transfer type excited states (29, 32, 33). These calculations have shown some success in the interpretation of the excimer emission. However, in these calculations, computational simplifications have been often used. Because of these approximations, there remain unsatisfactory features in the theoretical analyses (34).

In last few years, the fluorescence of some aromatic hydrocarbons was found to be quenched by some aromatic tertiary amines, e.g., N,N-dimethylaniline and N,N-dimethyltoluidine, in a number of solvents (35-37). In non-polar solvents, a broad and structureless emission band, redshifted from the fluorescence of the aromatic hydrocarbons, was observed. This anomalous fluorescence increases in intensity with increasing amine concentrations at the expense of the fluorescence intensity of the hydrocarbons. Through flash photolysis observations of cation and anion radicals, the quenching mechanism was demonstrated, in some cases, to be an electron transfer from the donor (amine) to the acceptor (hydrocarbon) (37c, 39). From the relationships among the frequencies of these anomalous fluorescence bands, the electron affinities of the excited hydrocarbons and the ionization potentials of the amines, Mataga and Ezumi thought this anomalous fluorescence to be

a kind of charge-transfer fluorescence (35d). From study of the frequency variation with the change of solvents, it was inferred that the "hetero-excimer" has a large dipole moment -- a further evidence of the charge-transfer nature of "hetero-excimers" (35b-c, 37c-d).

In fluorescence quenching studies of aromatic hydrocarbons by aliphatic amines in solution, it is found that all three kinds of aliphatic amines are excited singlet quenchers. Tertiary, but not primary and secondary, amines not only quench but form fluorescent complexes with a number of hydrocarbons, such as benzene, naphthalene, fluorene, etc. (38).

In the presence of tertiary aliphatic amines (triethylamine and N-methylpiperidine are used in the present studies), the hydrocarbon fluorescence is quenched, and broad and structureless emission bands appear at longer wavelengths. However, no change in the absorption spectrum is observed in the presence of amine. This suggests that the species responsible for this anomalous emission is only stable in the excited state.

Kinetic studies indicate that this anomalous emission is due to the exciplex* formed by the association of an

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*The nomenclature of "exciplex" is used here and henceforth, instead of "mixed excimer" and "hetero-excimer".

excited singlet aromatic hydrocarbon molecule with one tertiary amine molecule.

Furthermore, it is demonstrated that the exciplex is probably stabilized by partial electron-transfer from the amine molecules to the excited aromatic hydrocarbon molecules. This conclusion is based on study of the effects of substituents on the frequencies of this anomalous emission.

The significance of this discovery in the theories of the excimer is obvious. Since the lowest excited state of the hydrocarbon and that of tertiary amine are far from degenerate in energy, negligible exciton splitting is expected in this kind of exciplex.

A model study indicates that the stability of the exciplex is basically dependent upon the electron-transfer configuration, i.e., through Coulombic interaction. However, the red shift of the exciplex emission frequency is not only due to the stabilization energy of the exciplex but also to the fact that fluorescence produces an unbound pair of ground state monomer molecules. According to the Franck-Condon principle, the ground state pair will be produced in a condition of strain induced by the packing of surrounding solvent molecules appropriate for the exciplex. This "packing strain" will raise the energy of the final state

of the radiative decay and thereby shift the emission to larger wavelengths than would be the case in the vapour phase.

RESULTS

Mechanism of Fluorescence Quenching by Tertiary Aliphatic Amines

Many kinds of organic compounds have been found to influence fluorescence when added to solutions of aromatic hydrocarbons. The addition of these foreign substances may enhance, quench or shift the original fluorescence.

At room temperature, tertiary aliphatic amines are found to have the latter two effects when added to solutions of some aromatic hydrocarbons. As the concentration of the amine increases, the fluorescence intensity of the hydrocarbon decreases, and simultaneously a new emission band is observed. This new band is very broad, structureless and red-shifted from that of the original hydrocarbon. Initially as the concentration of the amine increases, the intensity of this new emission increases at the expense of the original hydrocarbon fluorescence. An additional increase on the quencher concentration results in reduction of the intensity of the new emission also. No new absorption bands are detected in these solutions.

These experimental observations suggest the quenching mechanism outlined in equations 7-13. The new emission is attributed to the exciplex, HA^*, which is formed in the quenching process.

$H^* \xrightarrow{k_{fH}} H + h\nu_H$	Fluorescence of H^*	(7)
$H^* \xrightarrow{k_{rH}} H$	Non-radiative decay	(8)
$H^* + A \xrightarrow{k_{HA}} HA^*$	Exciplex formation	(9)
$HA^* \xrightarrow{k_{fHA}} H + A + h\nu_{HA}$	Fluorescence of exciplex	(10)
$HA^* \xrightarrow{k_{rHA}} H + A$	Non-radiative decay	(11)
$HA^* \xrightarrow{k_{dHA}} H + A$	Regeneration of H^* from dissociation of exciplex	(12)
$HA^* + A \xrightarrow{k_{qHA}} H + A + A$	Quenching of exciplex	(13)

In this scheme, the tertiary aliphatic amine, A, can quench both the excited singlet hydrocarbon molecule, H^*, and the exciplex, HA^*. We believe that different quenching mechanisms, which will be covered in detail in the discussion section, are involved. Consequently, the quenching efficiencies of the amine towards these two excited species are different. As will be shown later, the quenching of the exciplex fluorescence is less efficient than the quenching of H^*. Therefore, at low concentrations of the quencher, quenching of the exciplex (equation 13) is too slow to compete with other fast decay processes

(equations 10-12) and consequently it can be neglected.

Considering only equations 7-12, we derive several relations either through direct solution of the differential equations or using the steady state assumption:

$$\frac{\Phi^{o}_{fH}}{\Phi_{fH}} = 1 + \frac{C}{C_{\frac{1}{2}}} = 1 + S_1 C, \tag{14}$$

$$\frac{\Phi_{fHA}}{\Phi_{fH}} = \frac{\Phi'_{fHA}}{\Phi^{o}_{fH}} \frac{C}{C_{\frac{1}{2}}} = S_2 C, \tag{15}$$

$$\frac{1}{\Phi_{fHA}} = \frac{1}{\Phi'_{fHA}} + \frac{C_{\frac{1}{2}}}{\Phi'_{fHA}} \frac{1}{C}, \tag{16}$$

$$C_{\frac{1}{2}} = \frac{(k_{fH} + k_{rH})\,(k_{fHA} + k_{rHA} + k_{dHA})}{k_{HA}\,(k_{fHA} + k_{rHA})}, \tag{17}$$

$$\Phi^{o}_{fH} = k_{fH}/(k_{fH} + k_{rH}),$$

$$\Phi'_{fHA} = k_{fHA}/(k_{fHA} + k_{rHA}), \tag{18}$$

where Φ^{o}_{fH} is the absolute quantum yield of the hydrocarbon fluorescence without addition of quencher, and Φ'_{fHA} is the hypothetical quantum yield of the fluorescence of the exciplex at the infinite concentration of the amine quencher

with the assumption that the quencher does not quench the exciplex fluorescence. Φ_{fH} and Φ_{fHA} are the quantum yields of the hydrocarbon and the exciplex respectively at the quencher concentration C.

In practive, however, measurement of the absolute quantum yield is difficult. A common experimental analysis of fluorescence quenching makes use of the assumption that the area under the spectral trace is proportional to the absolute quantum yield. Thus both Φ^{o}_{fH}/Φ_{fH} and Φ_{fHA}/Φ_{fH} are equal to the corresponding area ratios, A^{o}_{fH}/A_{fH} and A_{fHA}/A_{fH}. These values can be directly determined from the emission spectra.

As an example, Figure I shows the naphthalene fluorescence quenched by triethylamine. Figure II shows that there is no new absorption band observed in these solutions. Figures III and IV show the linear plots of equations 14 and 15. Table I summarizes all the quenching data for naphthalene, some of its derivatives and fluorene, with triethylamine and N-methylpiperidine as quenchers*.

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*For the fluorene with N-methylpiperidine case, non-linearity is exhibited. In the calculation of the rate parameters the limiting slopes at quencher concentrations equal to zero are used.

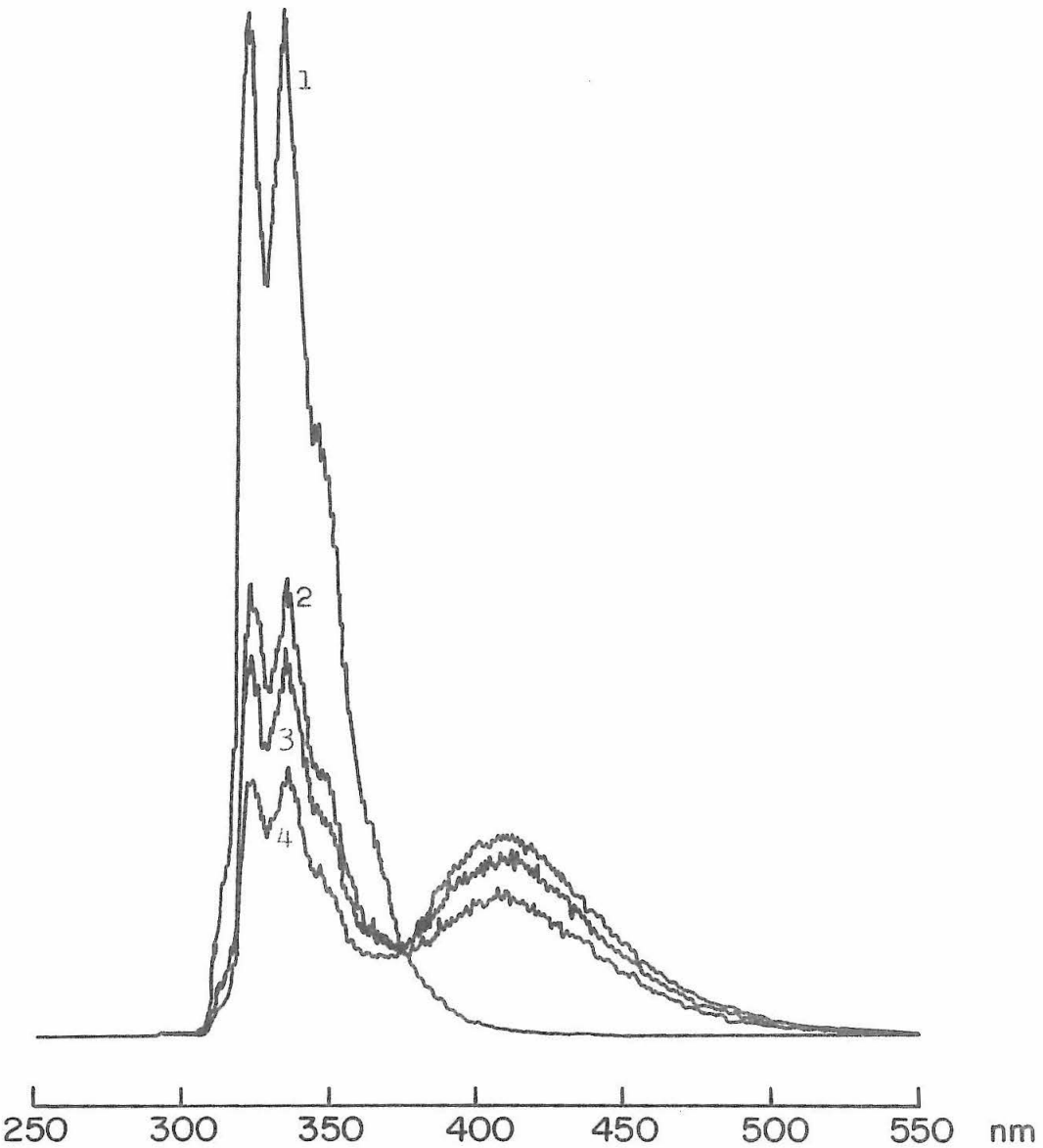

FIGURE I: Emission Spectra of Naphthalene in Cyclohexane in the Presence of Triethylamine (1-0; 2-5.86×10^{-3}; 3-8.79×10^{-3}; 4-14.65×10^{-3} mole/l).

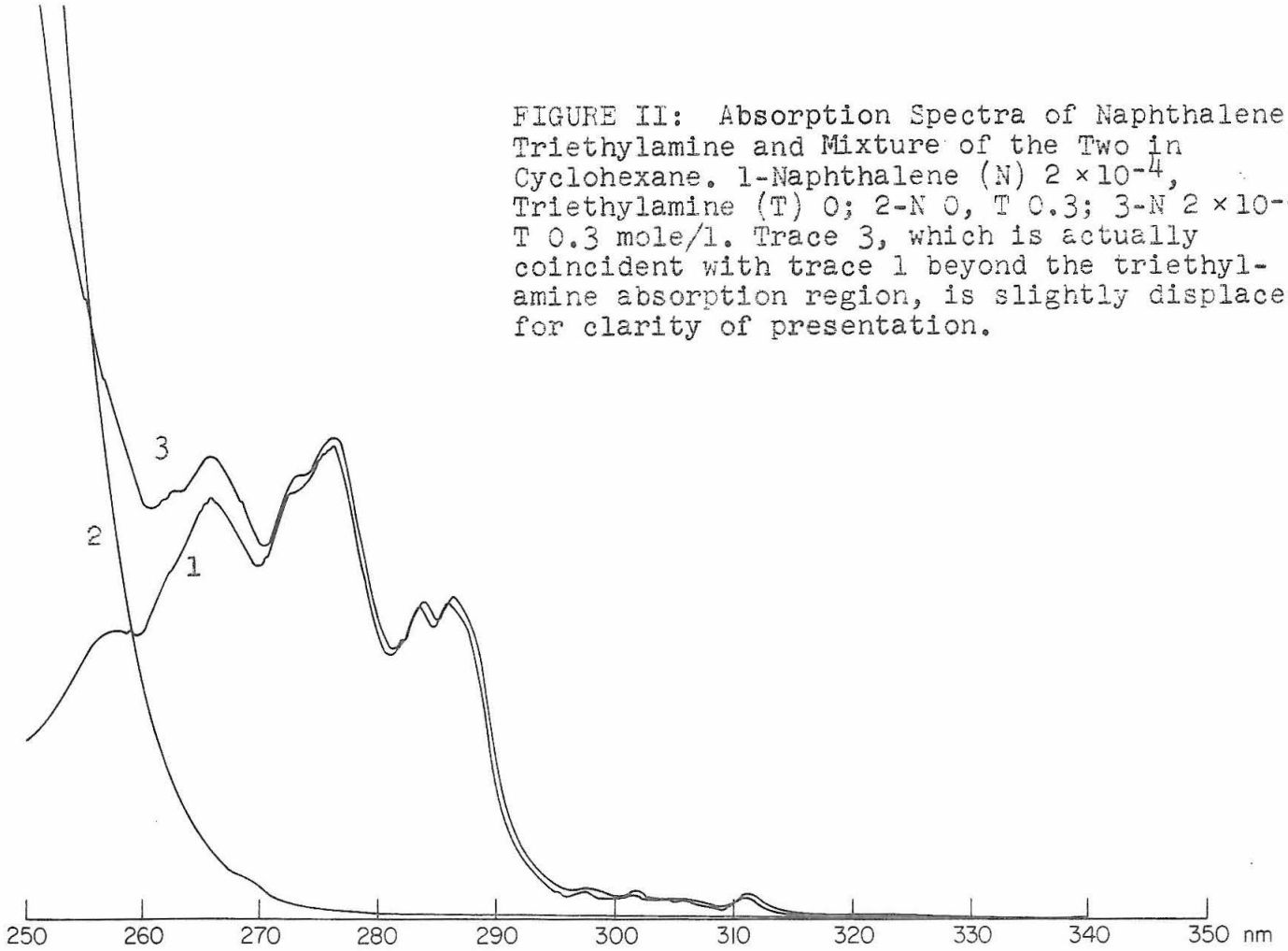

FIGURE II: Absorption Spectra of Naphthalene, Triethylamine and Mixture of the Two in Cyclohexane. 1-Naphthalene (N) 2×10^{-4}, Triethylamine (T) 0; 2-N 0, T 0.3; 3-N 2×10^{-4}, T 0.3 mole/l. Trace 3, which is actually coincident with trace 1 beyond the triethylamine absorption region, is slightly displaced for clarity of presentation.

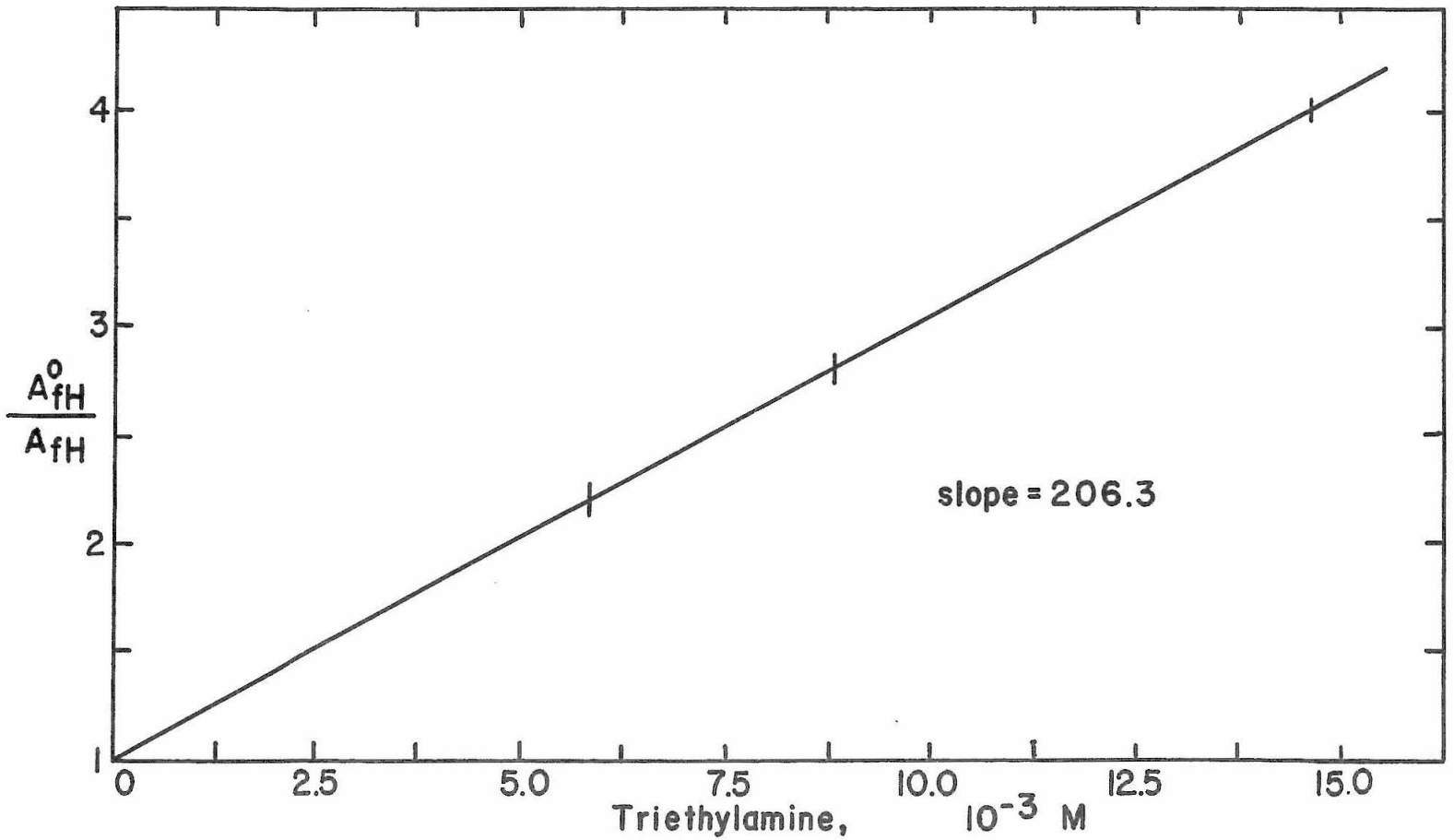

FIGURE III: Modified Stern-Volmer Treatment of Data from Figure I.

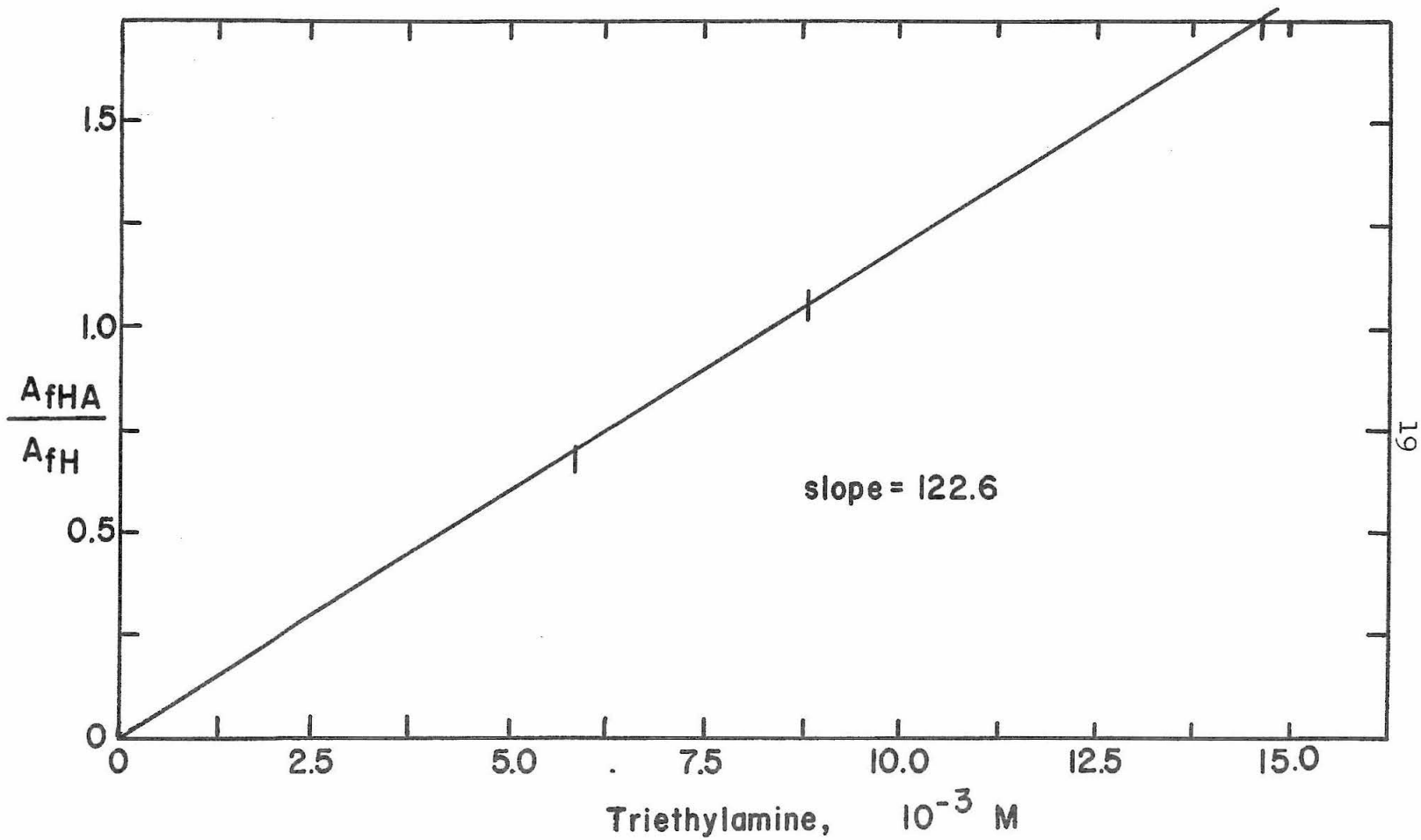

FIGURE IV: Ratio of Exciplex Fluorescence Quantum Yield to Hydrocarbon's as a Function of Triethylamine Concentration.

TABLE I

Fluorescence Quenching of Aromatic Hydrocarbons by Tertiary Aliphatic Amines

Quencher: Triethylamine

Hydrocarbon [a]	Quencher Concentration	$\frac{A_{fH}^{o}}{A_{fH}}$ [b]	$\frac{A_{fHA}}{A_{fH}}$ [b]
Naphthalene	0.00×10^{-3} M	1.00	0.00
	5.86	2.32	0.67
	8.79	2.82	1.05
	14.65	4.03	1.75
β-Fluoro-naphthalene	0.00×10^{-3} M	1.00	0.00
	4.99	1.38	0.18
	8.35	1.55	0.29
	9.98	1.80	0.38
	12.53	1.94	0.45
	14.97	2.32	0.57
	16.70	2.28	0.57
	19.95	2.79	0.80
	20.88	2.66	0.74

Table I (continued)

β-Chloro-naphthalene	0.00×10^{-2}	M	1.00	0.00
	2.26		1.31	1.23
	4.52		1.61	2.29
	6.78		2.02	3.28
β-Methyl-naphthalene	0.00×10^{-2}	M	1.00	0.00
	3.67		1.31	0.18
	4.99		1.43	0.24
	7.34		1.63	0.33
Fluorene	0.00×10^{-2}	M	1.00	0.00
	3.07		1.37	0.36
	6.13		1.74	0.72
	9.20		2.22	1.08

Quencher: N-methylpiperidine

Naphthalene	0.00×10^{-2}	M	1.00	0.00
	1.72		1.57	0.35
	3.43		1.98	0.71
	5.16		2.80	1.06
	6.88		3.19	1.52
	8.60		3.81	1.86

Table I (continued)

Fluorene [c]	0.00×10^{-2} M	1.00	0.00
	5.94	1.12	0.10
	11.89	1.24	0.19
	17.83	1.43	0.29
	23.77	1.75	0.38
	29.71	1.91	0.45
	35.66	2.26	0.52
	41.60	2.63	0.60

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a. Appropriate concentrations of aromatic hydrocarbons are used to insure that no concentration quenching occurs.
b. All values are average values.
c. The non-linearity exhibited in the case of fluorene quenched by N-methylpiperidine may be due to large k_{qHA}. The rate parameters are later calculated with the limiting slopes at quencher concentrations of zero.

In order to interpret equation 16 experimentally, the absolute fluorescence quantum yield of the exciplex must be known. This quantum yield can be obtained by comparison of the area under the exciplex emission portion of the spectrum with the area under the spectrum of the unquenched hydrocarbon, which is of known fluorescence quantum yield, under the same experimental conditions. Equation 16 can be modified to:

$$\frac{1}{A_{fHA}} = \frac{\Phi^{o}_{fH}}{\Phi'_{fHA}\, A^{o}_{fH}} + \frac{\Phi^{o}_{fH}}{A^{o}_{fH}} \frac{C_{\frac{1}{2}}}{\Phi'_{fHA}} \frac{1}{C} \qquad (19)$$

where all symbols are ginen on pages 14-15.

Figure V shows that this relation is also satisfied at low concentrations of the quencher.

At very high concentrations of the quencher, the fluorescence of the aromatic hydrocarbon is almost completely quenched. This is obviously due to the fact that quencher molecules are in the immediate vicinity of the hydrocarbon molecules just when they are excited by irradiation. Immediate quenching of the excited hydrocarbon molecules is followed by the formation of the fluorescent exciplex. Consequently, this situation is equivalent to the direct excitation of the exciplex just as if a ground state of the exciplex existed. As a result, the decay pro-

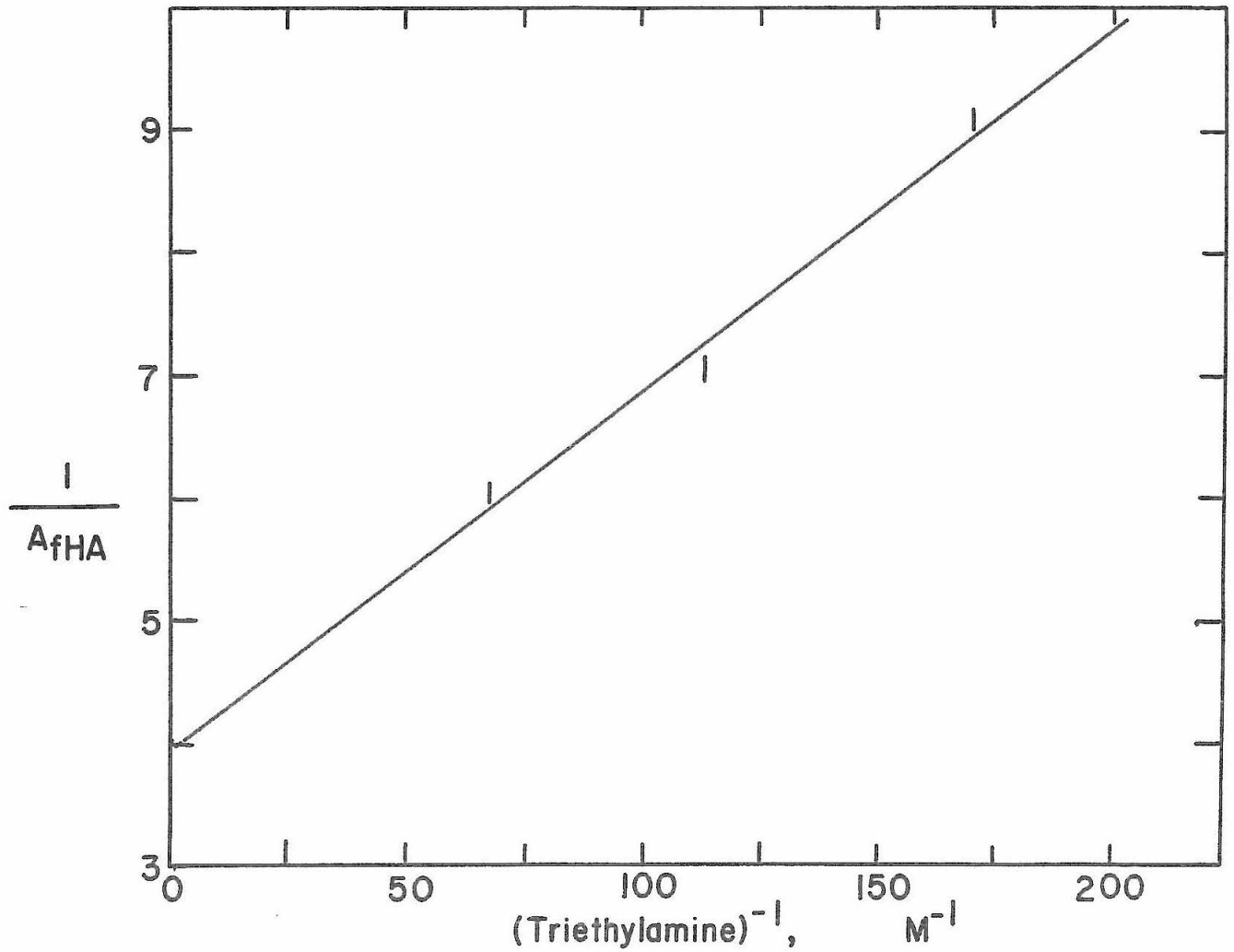


FIGURE V: Reciprocal of Relative Exciplex Fluorescence Quantum Yield as a Function of Reciprocal of Triethylamine Concentration.

cesses following the excitation are those shown in equations 10-13.

This rationale is validated by the observation that the decay of the exciplex fluorescence is purely exponential, in contrast to the non-exponential decay at low concentrations of the quencher. Thus the decay of the exciplex fluorescence at high quencher concentrations can be expressed as:

$$I = I_o \exp\left\{-(k_{fHA} + k_{rHA} + k_{dHA} + k_{qHA}\, C)\, t\right\}$$

$$= I_o \exp\left\{-(t/\tau_{HA})\right\}$$

or

$$1/\tau_{HA} = k_{fHA} + k_{rHA} + k_{dHA} + k_{qHA}\, C$$

$$= 1/\tau^{o}_{HA} + S_3\, C \qquad (20)$$

This linear relation is confirmed experimentally and is shown in Figure VI and Table II.

In the intermediate quencher concentration range, all decay processes are of comparable importance. From all of equations 7-13, the following expression for the fluoscence quantum yield of the exciplex can be obtained.

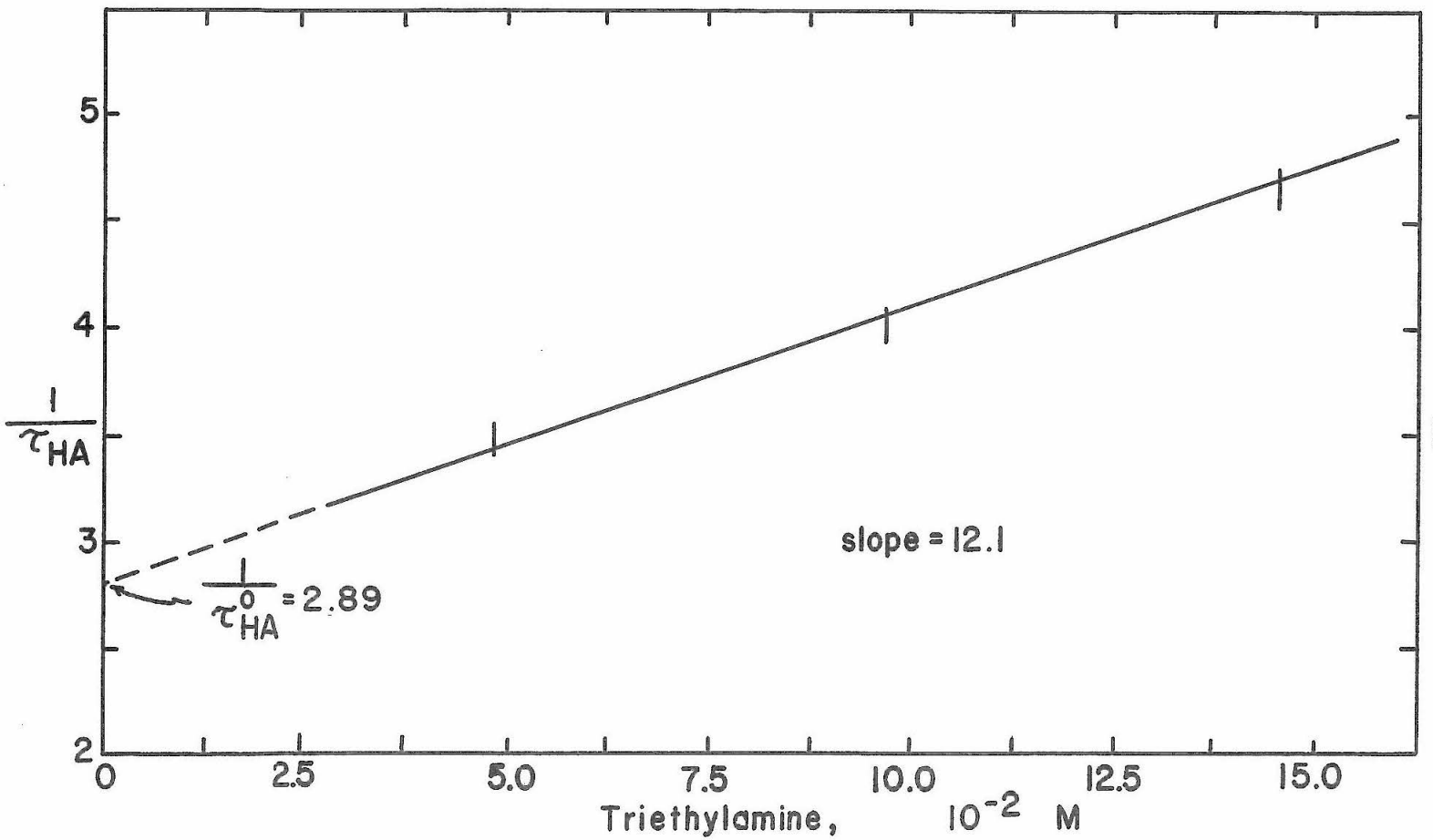


FIGURE VI: Exciplex Decay Constant against Triethylamine Concentration.

TABLE II

Fluorescence Lifetimes of Exciplexes at Different Concentrations of Quencher[a].

Quencher: Triethylamine

Hydrocarbon	Quencher Concentration	Lifetime of Hydrocarbon[b] in nanosec.	Lifetime of Exciplex[b] in nanosec.	Decay Rate in sec^{-1}
Naphthalene	0.00×10^{-2} M	101.667		
	4.86		28.625	3.49×10^{7}
	9.71		24.825	4.03
	14.57		21.425	4.67
β-Fluoro-naphthalene	0.00×10^{-2} M	12.54		
	4.83		16.79	5.96×10^{7}
	9.66		14.75	6.78
	14.50		13.46	7.43
	19.33		12.18	8.21

Table II (continued)

β-Chloro-naphthalene	0.00×10^{-2} M	3.94		
	4.89		5.00	2.00×10^{7}
	9.78		3.93	2.55
	14.67		2.96	3.38
	19.56		2.50	4.00
β-Methyl-naphthalene	0.00 M	25.68		
	0.49		16.15	6.20×10^{7}
	0.98		10.45	9.57
	1.47		8.73	11.44
	1.96		7.25	13.79
Fluorene	0.00×10^{-1} M	6.23		
	4.03		6.53	1.53×10^{8}
	8.05		5.74	1.74
	12.08		5.14	1.95
	16.11		4.69	2.13

Table II (continued)

Quencher: N-Methylpiperidine.

Naphthalene	0.00	M	101.67		
	0.25			17.20	0.98×10^7
	0.50			12.10	5.81
	0.76			9.83	10.17
Fluorene	0.00	M	6.58		
	0.50			6.70	1.49×10^8
	1.00			4.77	2.10
	1.51			3.85	2.60
	2.02			3.18	3.14

a. Exciplex fluorescence lifetimes were measured with a filter which is opaque to the hydrocarbon emission.
b. All values are average values.

$$\Phi_{fHA} = \frac{k_{HA}\, C}{k_{fH} + k_{rH} + k_{HA}\, C} \cdot \frac{k_{fHA}}{k_{fHA} + k_{rHA} + k_{qHA}\, C + V\, k_{dHA}},$$

$$V = \frac{k_{fH} + k_{rH}}{k_{fH} + k_{rH} + k_{HA}\, C}. \qquad (21)$$

In equation 21, the first term is the ratio of the exciplex formation rate to the total rate of decay processes from the excited hydrocarbon molecules. In the second term, $V\, k_{dHA}$ is the effective non-radiative decay of exciplexes through dissociation. Thus the second term is the ratio of the exciplex fluorescence rate to the sum of all exciplex decay rates.

Differentiating equation 21 with respect to quencher concentration, we can obtain the concentration of quencher giving the maximum exciplex fluorescence quantum yield, C_{Max}.

$$C_{Max}^2 = \frac{(k_{fH} + k_{rH})\,(k_{fHA} + k_{rHA} + k_{dHA})}{k_{HA}\, k_{qHA}}. \qquad (22)$$

This maximum can be experimentally determined by plotting A_{fHA} against the concentration of the quencher as in Figure VII.

All these experimental data indicate that the exciplex is really the cause of the red-shifted, broad and

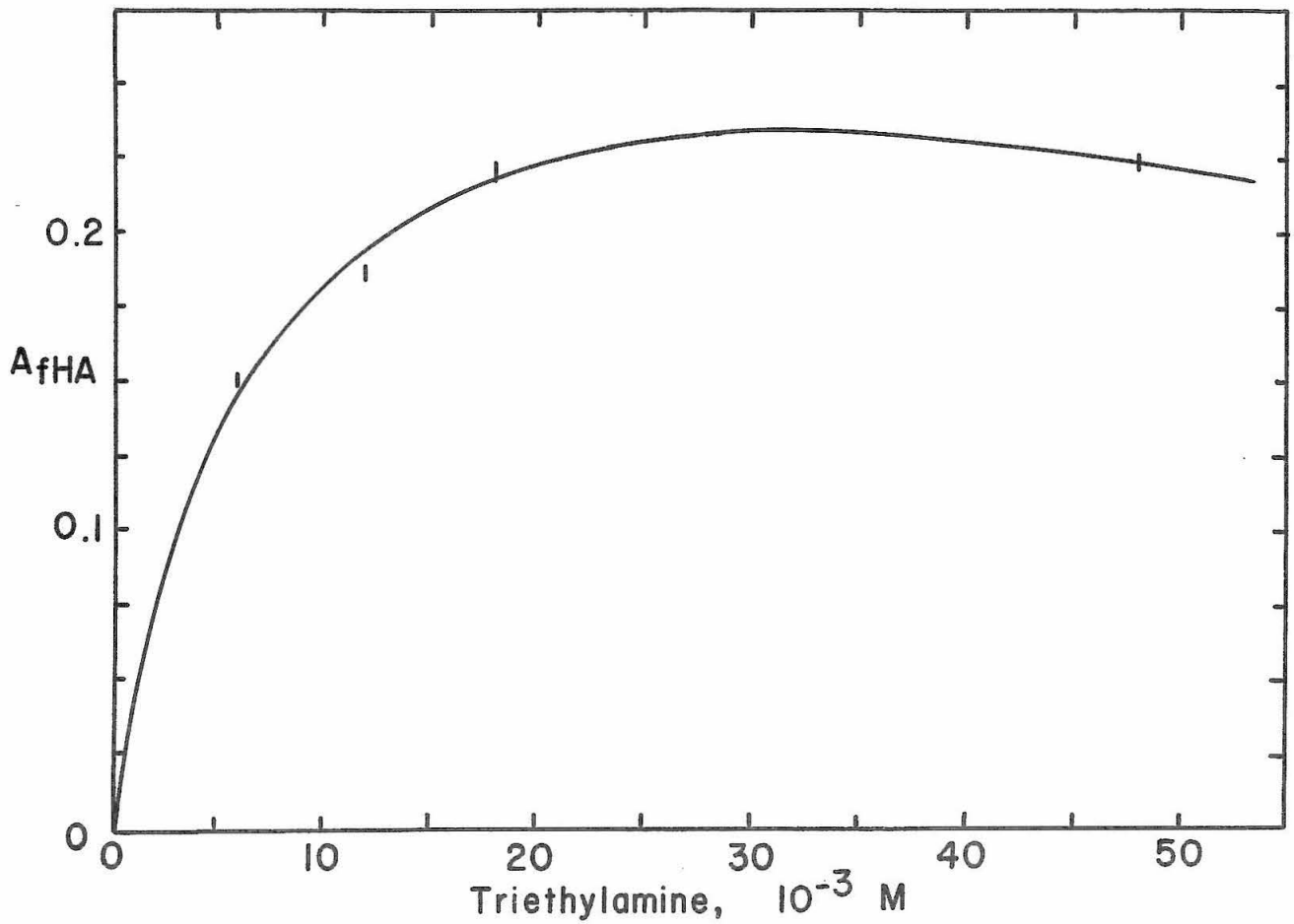


FIGURE VII: Relative Exciplex Fluorescence Quantum Yield as a Function of Triethylamine Concentration.

structureless emission bands.

This is further confirmed by eliminating the possibility that the band is due to photo-products produced from the aromatic hydrocarbon and amine upon irradiation. All of samples investigated were then irradiated by a pyrex-filtered Hanovia 450W medium pressure mercury lamp for half a day and still gave the same quenching data they had given before.

Fluorescence Quantum Yields of Aromatic Hydrocarbons

All these kinetic studies were carried out in purified cyclohexane solvent. Fluorescence quantum yields of many hydrocarbons in this solvent are available in the literature. Naphthalene (0.23), fluorene (0.80) and β-methylnaphthalene (0.32) are used here (40). For β-fluoronaphthalene and β-chloronaphthalene, a comparison method is used with naphthalene as the reference compound (41). Reasonable values are obtained, 0.75 for β-fluoronaphthalene and 0.058 for β-chloronaphthalene.

Determination of Rate Parameters

With the data shown above, the rate parameters in equations 7-13 can be determined.

It is assumed that the lifetime of the hydrocarbon in the absence of the quencher is represented τ_H^o, which can be experimentally measured. The values are shown in Table II along with the lifetimes of their exciplexes at different concentrations of the quencher.

All rate parameters in equations 7-13 can be expressed in terms of experimentally determinable values. Using the symbols in equations 14, 15, 20 and 22, they are as follows:

$$k_{fH} = \Phi_{fH}^o / \tau_H^o$$

$$k_{rH} = (1 - \Phi_{fH}^o) / \tau_H^o$$

$$k_{HA} = 1/(\tau_H^o \cdot S_3 \cdot C_{Max}^2 \cdot \tau_{HA}^o)$$

$$k_{fHA} = S_3 \cdot S_2 \cdot \Phi_{fH}^o \cdot C_{Max}^2$$

$$k_{rHA} = S_3 \cdot C_{Max}^2 \cdot (S_1 - S_2 \cdot \Phi_{fH}^o)$$

$$k_{dHA} = (1/\tau_{HA}^o) - S_3 \cdot S_1 \cdot C_{Max}^2$$

$$k_{qHA} = S_3$$

Rate parameters for the exciplex formation of

naphthalene, substituted naphthalenes and fluorene with triethylamine along with those for naphthalene and fluorene with N-methylpiperidine, are calculated and summarized in Table III. The significance of these numbers will be covered in the discussion section.

TABLE III

Rate Parameters in Fluorescence Quenching Processes of Aromatic Hydrocarbons by Tertiary Amines [a]

Quencher: Triethylamine

Hydrocarbon	k_{fH}	k_{rH}	k_{HA}	k_{fHA}	k_{rHA}	k_{dHA}	k_{qHA}
Naphthalene	0.23	0.76	226.66	0.35	2.23	0.30	12.10
β-Fluoro-naphthalene	5.98	1.99	1344.95	0.94	1.71	2.59	15.34
β-Chloro-naphthalene	1.47	23.91	876.26	1.12	4.37	7.23	13.97
β-Methyl-naphthalene	1.25	2.65	36.24	0.57	3.17	0.34	5.04
Fluorene	12.84	3.21	1120.99	1.82	0.07	10.83	4.98

Quencher: N-Methylpiperidine

Naphthalene	0.23	0.76	35.10	0.53	2.89	0.30	8.64
Fluorene	12.15 [b]	3.04 [b]	129.83	1.55	0.29	7.89	10.81

Table III (continued)

a. All rate parameters (equations 7-13) are expressed in 10^7 sec^{-1} except k_{HA} and k_{qHA} in 10^7 sec^{-1} M^{-1}.

b. The differences of these values from those in the fluorene and triethylamine systems are due to the different degree in degassing of samples.

Exciplexes of Aromatic Hydrocarbons with Triethylamine

The fluorescences of many aromatic hydrocarbons can be quenched by triethylamine. Some hydrocarbons exhibit the exciplex emissions with triethylamine while others show the quenching phenomenon only.

All these experiments were carried out in pure triethylamine or in a mixture of triethylamine with cyclohexane. The results are summarized in Table IV.

No difference can be observed in the absorption spectra beyond the triethylamine cut-off frequency.

The exciplex emissions of some compounds, such as naphthalene and fluorene, can be readily observed in cyclohexane with a small amount of triethylamine, while no emission can be found at all in pure triethylamine. The lack of exciplex emissions in pure triethylamine are due to the complete quenching of the exciplex.

The exciplex emissions of several other compounds can be found in both pure triethylamine and in a mixture of triethylamine and cyclohexane. There is a difference in the maxima of their exciplex emission bands (Table IV). This is due to the solvent effect and will be shown in the later section.

Lastly, several compounds show no exciplex emission and only very inefficient fluorescence quenching in tri-

ethylamine. Phenanthrene, for example, even shows its own characteristic emission spectrum in pure triethylamine.

From Table IV, it is obvious that the electron affinity of the aromatic hydrocarbon is not the only property which determines the formation of exciplex. The fluorescence of hydrocarbons with high electron affinity are not necessarily more effectively quenched nor do these compounds seem to form exciplexes. There are other factors involved in the exciplex formation.

TABLE IV

Exciplexes of Aromatic Hydrocarbons with Triethylamine [a]

Hydrocarbon (Electron Affinity) [b]	In Cyclohexane-Triethylamine Mixture [c]		In Pure Triethylamine	
	Quenching	Exciplex Emission (maximum)	Quenching	Exciplex Emission (maximum)
Benzene (- 1.5)	EQ	Yes (345.0)	CQ	No
Toluene	EQ	Yes (347.0)	CQ	No
Biphenyl (- 0.5)	EQ	Yes (403.3)	CQ	No
Naphthalene (- 0.3)	EQ	Yes (409.8)	CQ	No
Fluorene	EQ	Yes (385.7)	CQ	No
Carbazole [d]	IQ	No	IQ	No
N-Methylcarbazole	IQ	No	IQ	No
Dibenzofuran	IQ	Yes (406.0)	IQ	Yes (414.8)
Anthracene (0.5)	EQ	No	CQ	No
Phenanthrene (0.1)	IQ	No	IQ	No

Table IV (continued)

Triphenylene (- 0.05)	IQ	No	CQ	No
Chrysene (0.3)	IQ	No	IQ	No
Perylene (0.85)	IQ	No	IQ	No
t-Stilbene	EQ	Yes (445.8)	CQ	No
β-Styrylnaphthalene	EQ	Yes (456.6)	CQ	No

a. Symbols in this Table are as follows: EQ, efficient fluorescence quenching of hydrocarbon; IQ, inefficient quenching; CQ, complete quenching; Yes, exciplex emission observable with emission maximum in nm included in the parenthesis; and No, exciplex emission not observable.

b. in eV. From G. Briegleb, Angew. Chem., International Ed., 3, 617 (1964).

c. Enough triethylamine was added into hydrocarbon solution in cyclohexane to give observable exciplex emission maximum when it exists.

d. Hydrocarbon emission is red-shifted about 900 cm^{-1} for both solvent systems with no change of the shape. It results from the hydrogen bonding effect.

Exciplexes of Substituted Naphthalenes with Triethylamine

The fluorescence quenching of substituted naphthalenes by triethylamine deserves a special attention because of its importance in the elucidation of the nature of the exciplex.

For those sterically crowded naphthalenes, the exciplex emission bands can only be observed clearly in pure triethylamine. No clear-cut exciplex emission maximum can be determined in a mixture of cyclohexane and triethylamine.

Table V summarizes all the results of substituted naphthalenes with triethylamine.

From this table, the dependence of the maximum of the exciplex emission upon the substituent group can be seen. The maxima not only change with the substituent groups but also with the position of the substituents on the aromatic skeleton. For instance, the exciplex emission maximum of α-naphthonitrile with triethylamine in cyclohexane is 477.4 nm and that of its β-isomer is 456.8 nm. Yet the positions of their hydrocarbon emissions do not differ significantly.

Some polymethyl-substituted naphthalenes exhibit exciplex emissions in cyclohexane and triethylamine mixture only when a large amount of triethylamine is added. Because of the difference of the amount of triethylamine added for

TABLE V

Exciplexes of Substituted Naphthalenes with Triethylamine [a]

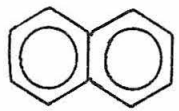
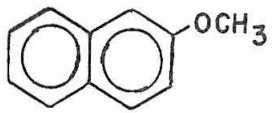
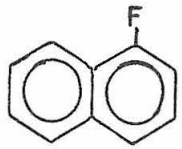
Substituted Naphthalenes	In Cyclohexane-Triethylamine Mixture [b]		In Pure Triethylamine	
	Quenching	Exciplex Emission (maximum)	Quenching	Exciplex Emission (maximum)
	EQ	Yes (409.81)	CQ	No
	IQ	No	IQ	No
	EQ	Yes (417.46)	CQ	No

Table V (continued)

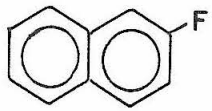
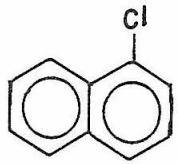
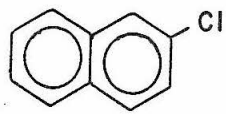
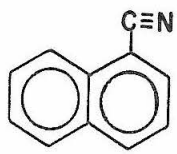
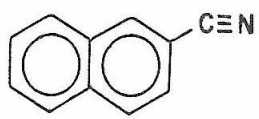
	EQ	Yes (416.93)	CQ	No
	EQ	Yes (432.56)	CQ	No
	EQ	Yes (425.04)	CQ	No
	EQ	Yes (477.40)	CQ	No
	EQ	Yes (456.84)	CQ	No

Table V (continued)

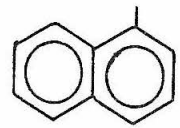
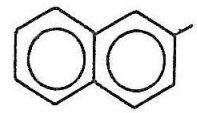
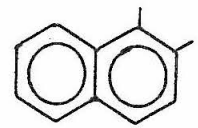
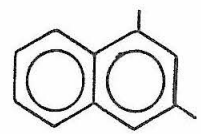
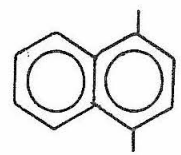
	EQ	Yes (406.11)	CQ	No
	EQ	Yes (407.60)	CQ	No
	IQ	Yes (411.50)	IQ	Yes (420.00)
	IQ	Yes (412.00)	IQ	Yes (420.00)
	IQ	Yes (410.00)	IQ	Yes (422.50)

Table V (continued)

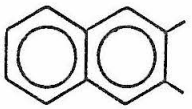
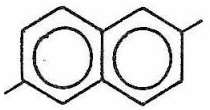
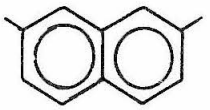
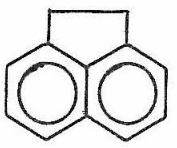
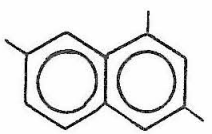
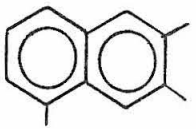
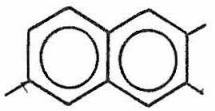
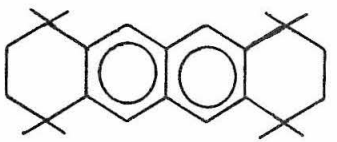
	IQ	Yes (411.00)	IQ	Yes (414.50)
	IQ	Yes (412.00)	IQ	Yes (415.00)
	IQ	Yes (407.00)	IQ	Yes (420.00)
	IQ	Yes (----)	IQ	Yes (411.50)
	IQ	Yes (----)	IQ	Yes (414.50)

Table V (continued)

	IQ	Yes (410.00)	IQ	Yes (415.00)
	IQ	Yes (----)	IQ	Yes (408.00)
	IQ	Yes (405.00)	IQ	Yes (411.00)

a. Same symbols are used in this table as Table IV.
b. For mono-substituted naphthalenes, triethylamine concentration is small, less than 0.01 M. For poly-substituted naphthalenes, large amount of triethylamine has to be added in order to give enough quenching. Comparison in the latter case is meaningless.

different compounds, it will be more meaningful to compare those values observed in pure triethylamine. Table V shows that generally the more sterically crowded substituted naphthalenes give exciplex emission bands with maxima at shorter wavelengths.

Solvent Effects on Maxima of Exciplex Emissions

The exciplex emission bands of aromatic hydrocarbons and triethylamine are very sensitive to the change of the environment of the exciplex. The solvent, as one of the enviromental factors, is investigated here.

The exciplex emission band changes with the solvent while the characteristic emission of the aromatic hydrocarbon does not. Three kinds of solvents have been used, i.e., saturated hydrocarbons (including some chlorohydrocarbons), unsaturated hydrocarbons and ethers.

The maxima of the exciplex emission bands is measured with reference to the mercury lines. Table VI lists the maxima of the exciplex emission bands and their red-shift values with respect to the hydrocarbon emissions for both the naphthalene-triethylamine and the fluorene-triethylamine exciplexes in different solvents. Figure VIII gives an example of the solvent effect on the exciplex emission maxima.

TABLE VI

Naphthalene-Triethylamine and Fluorene-Triethylamine [a, b] Exciplex Emission Maxima in Different Solvents

	Solvent	$(\tilde{\nu}_{Max})_{N-T}$ [c]	$(\tilde{\nu}_{Max})_{F-T}$ [c]	$(\Delta\tilde{\nu})_{N-T}$ [d]	$(\Delta\tilde{\nu})_{F-T}$ [d]
1.	n-Hexane	24639.0	26431.9	6092.4	5352.6
2.	n-Heptane	24571.8	26288.8	6159.6	5495.7
3.	Cyclopentane	-	26098.8	-	5685.7
4.	Cyclohexane	24398.6	25949.1	6332.8	5835.4
5.	Cyclohexene	24301.7	25827.1	6429.7	5957.4
6.	1,4-Cyclohexadiene	23567.7	24987.8	7163.7	6796.7
7.	Toluene	22781.3	24529.3	7950.1	7255.2
8.	Benzene	22715.4	24420.0	8016.0	7364.5
9.	n-Butyl ether	23377.1	24778.9	7354.3	7005.6
10.	Isopropyl ether	22945.1	24578.5	7786.3	7206.0
11.	Ethyl ether	22628.8	24413.7	8102.6	7370.8

Table VI (continued)

12. p-Dioxane	21979.5	23720.3	8751.9	7964.2
13. Tetrahydrofuran	21445.4	22842.5	9286.0	8942.0
14. 1,2-Dimethoxyethane	21262.1	22691.2	9469.3	9093.3
15. Dichloromethane	21321.1	22940.4	9410.3	8844.1
16. 1,1-Dichloroethane	21802.6	23631.9	8928.8	8152.6

a. Biphenyl-triethylamine exciplex emission maximum has been measured in three different solvents. Its emission maximum is 24795.5 in cyclohexane, 23244.5 in benzene and 22257.1 in p-dioxane, all in unit of cm^{-1}.

b. Exciplex emission maxima were determined with reference to the mercury lines.

c. Emission maxima are in cm^{-1}. Subscripts N-T and F-T denote the naphthalene-triethylamine and fluorene-triethylamine exciplexes respectively.

d. The red-shift value of the exciplex emission maximum from the fluorescence maximum of the hydrocarbon in cm^{-1}. Emission maximum of fluorene is 31784.5 cm^{-1} and that of naphthalene is 30731.4 cm^{-1}.

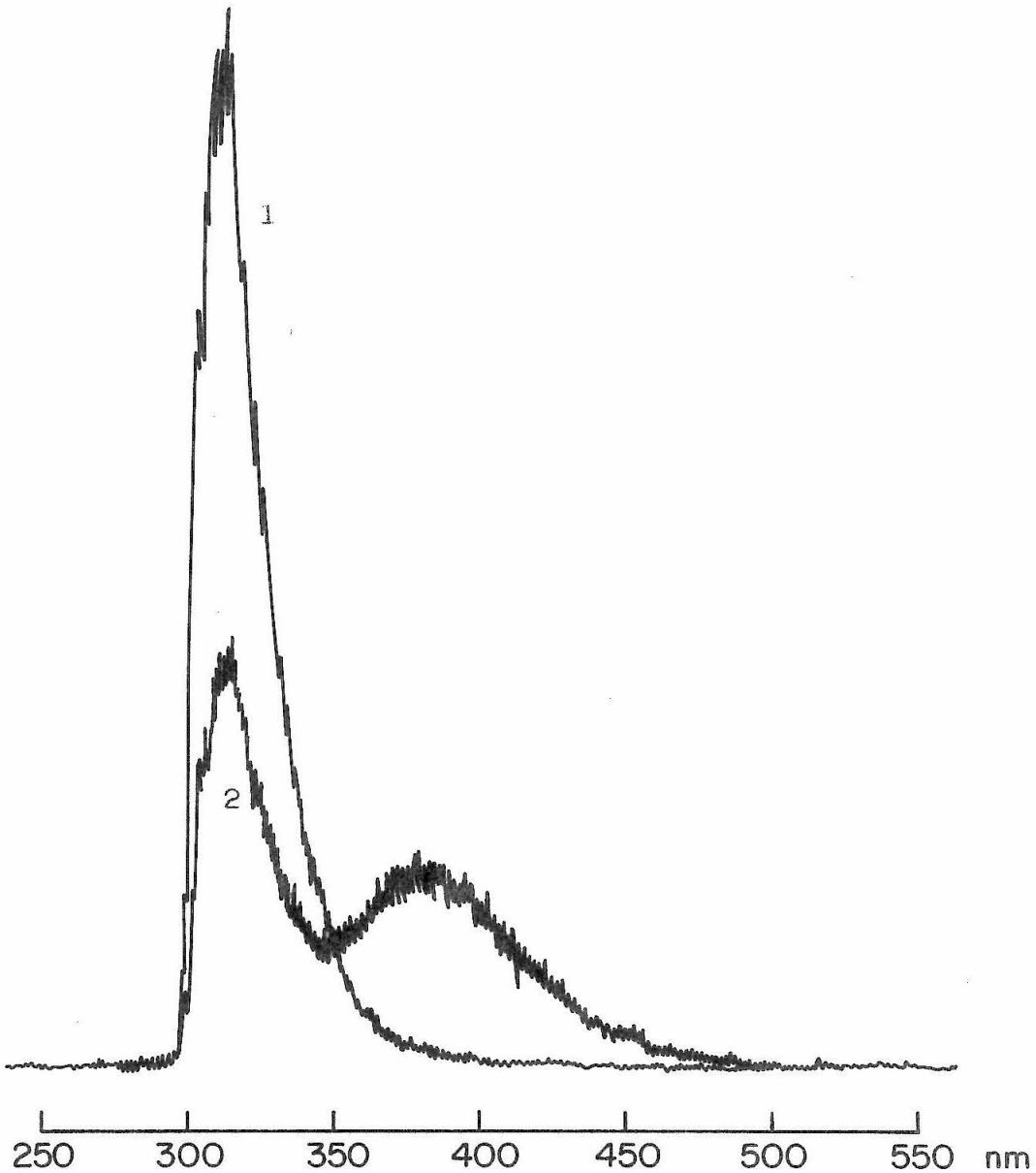


FIGURE VIIIa: Emission Spectra of Fluorene in n-Hexane in the Presence of Triethylamine (1-0; 2-0.17 mole/l).

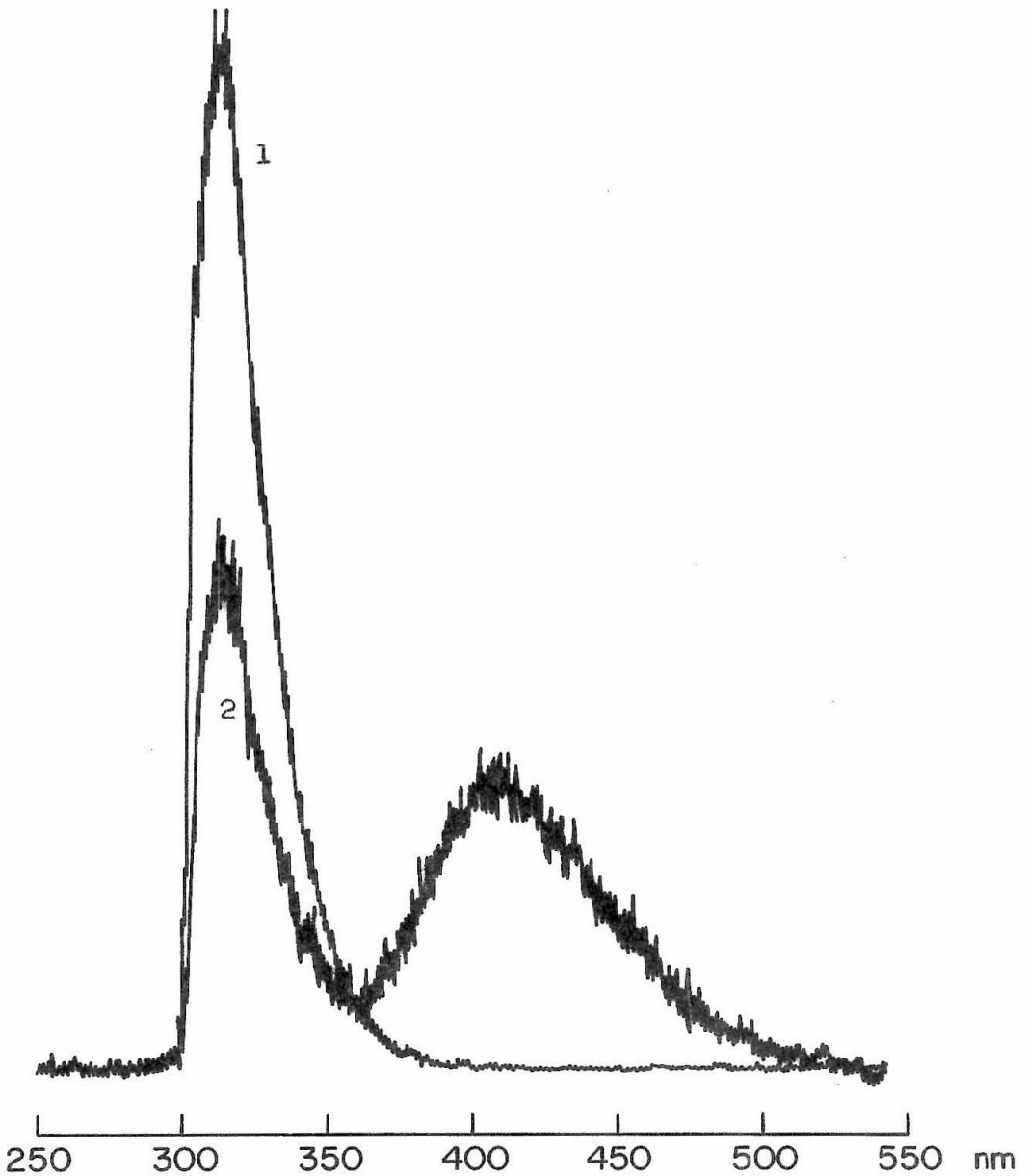


FIGURE VIIIb: Emission Spectra of Fluorene in Benzene in the Presence of Triethylamine (1-0; 2-0.18 mole/1). The vertical scale of trace 2 has been expanded by a factor of 10/3.

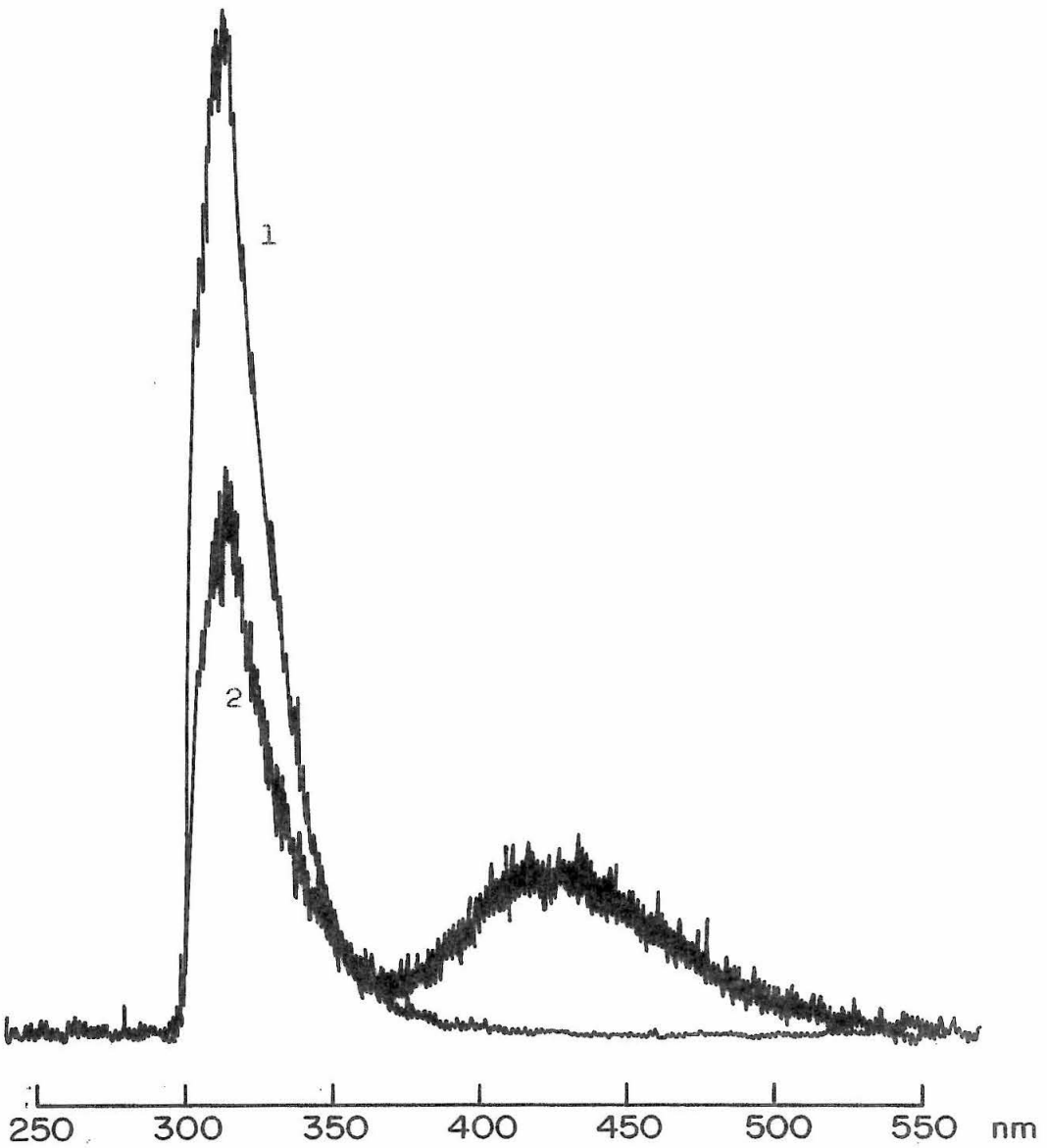


FIGURE VIIIc: Emission Spectra of Fluorene in p-Dioxane in the Presence of Triethylamine (1-0; 2-0.17 mole/1). The vertical scale of trace 2 has been expanded by a factor of 10/3.

By plotting the maxima of fluorene-triethylamine exciplex emission bands in different solvents against those of naphthalene-triethylamine in corresponding solvents (Figure IX), a linear relationship can be observed with a slope of 1.011.

Moreover, the red-shift values of these exciplex emission maxima from their corresponding hydrocarbon emissions are also linearly related with a slope of 1.006, (Figure X).

These two linear relationships suggest that solvents have nearly equal influence on the two exciplexes of the different components.

In general, the more polar the solvent, the larger the red-shift value of the exciplex emission maximum is.

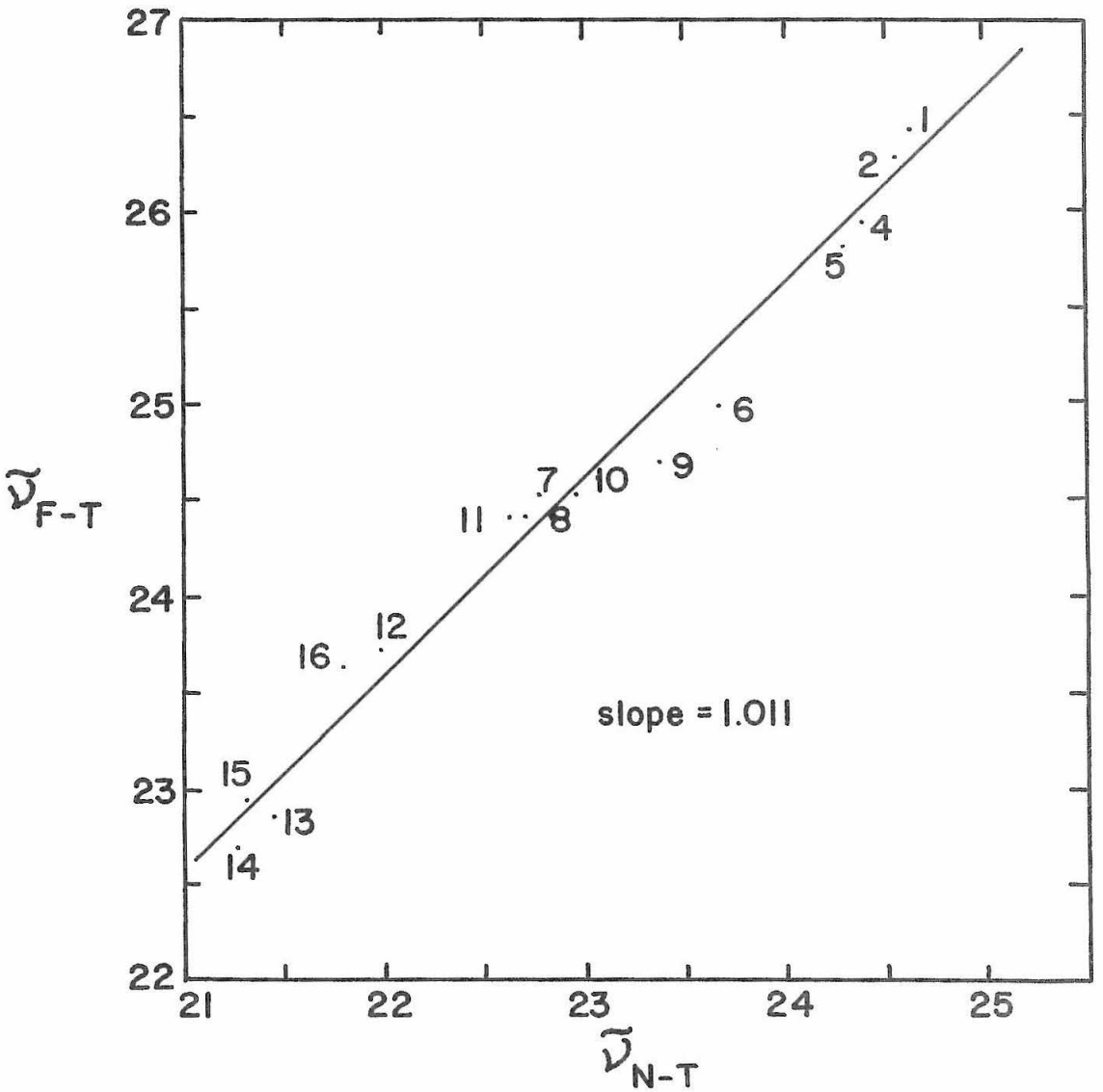


FIGURE IX: Fluorene-Triethylamine Exciplex Emission Maxima against Naphthalene-Triethylamine Exciplex Emission Maxima in Different Solvents. Both are in 1000 cm^{-1} units. (see Table VI)

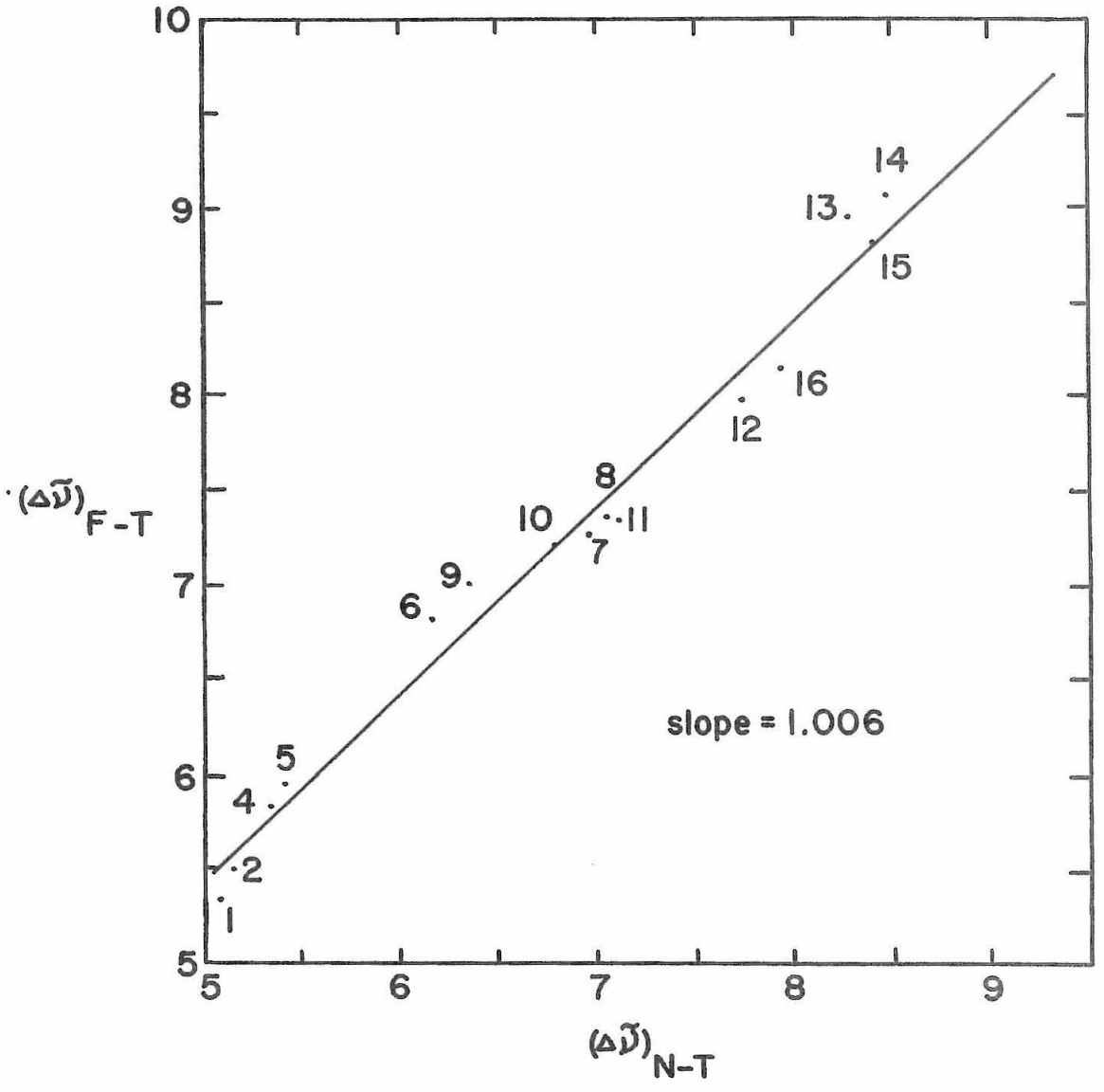


FIGURE X: Red-shift of Fluorene-Triethylamine Exciplex Emission against that of Naphthalene-Triethylamine Exciplex Emission in Different Solvents. Both are in 1000 cm^{-1} units. (see Table VI)

Exciplex Emissions in Mixed Solvents

As an extension of the solvent effect study, the changes of the naphthalene-triethylamine exciplex emission maxima in mixed solvents were investigated. Two mixed solvent systems are used, i.e., cyclohexane and p-dioxane, cyclohexane and tetrahydrofuran.

Tables VII and VIII list the maxima of naphthalene-triethylamine exciplex emission bands in different compositions of the mixed solvent systems. Figures XI and XII show the plots of the exciplex emission maxima against the molar fractions of the more polar component of the binary mixed solvents.

The non-linearity of these plots indicates that the composition in the vicinity of the exciplex is different from the bulk solution. The strong initial dependence of the frequency maxima of the exciplex upon the mole fractions of the polar component indicates that the polar solvent component is more involved in the change of the microscopic environment of the exciplex.

The ratio of the mole fractions in the vicinity of the exciplex, x_1/x_2, should be directly proportional to their ratio in the bulk solution, x_1^o/x_2^o. Following J. Padova (68), it is expressed as follows:

$$x_1/x_2 = x_1^o/x_2^o \; 10^a \qquad (23)$$

where a is the index of preferential solvation of the exciplex.

The solvation energy of the exciplex in mixed solvents with respect to the hypothetical exciplex in vapour phase, hc $\Delta\tilde{\nu}_{Mix}$, can be separated into two individual components, hc $\Delta\tilde{\nu}_1$ and hc $\Delta\tilde{\nu}_2$ as follows:

$$hc\,\Delta\tilde{\nu}_{Mix} = hc\,(x_1\,\Delta\tilde{\nu}_1 + x_2\,\Delta\tilde{\nu}_2)$$

or

$$\tilde{\nu}_{Mix} = (1 - x_2)\;\tilde{\nu}_1 + x_2\;\tilde{\nu}_2,$$

where all emission maxima are expressed in cm^{-1}. Substituted with equation 23, it can be modified as follows:

$$\tilde{\nu}_{Mix} = \frac{x_1^o\;\tilde{\nu}_1\;10^a + (1 - x_1^o)\;\tilde{\nu}_2}{1 + (10^a - 1)\;x_1^o}\;. \qquad (24)$$

The limiting values of $\tilde{\nu}_{Mix}$ for x_1^o approaching zero and unity are $\tilde{\nu}_2$ and $\tilde{\nu}_1$, respectively.

Taking the differentiation of equation 24 with respect to x_1^o,

$$\frac{\partial\tilde{\nu}_{Mix}}{\partial x_1^o} = \frac{(\tilde{\nu}_1 - \tilde{\nu}_2)\;10^a}{\left\{1 + (10^a - 1)\;x_1^o\right\}^2} \qquad (25)$$

The limiting values of $\partial \tilde{\nu}_{Mix}/\partial x_1^o$ for x_1^o approaching zero and unity are 10^{a} $(\tilde{\nu}_1 - \tilde{\nu}_2)$ and 10^{-a} $(\tilde{\nu}_1 - \tilde{\nu}_2)$ respectively. These are just the slopes of the curves, $\tilde{\nu}_{Mix}$ vs. x_1^o, at limiting values of $x_1^o \longrightarrow 0, 1$ (Figures XI and XII). These slopes can be obtained from these figures. The ratio of these two limiting slopes is 10^{2a}.

For naphthalene-triethylamine exciplex, a is equal to 0.33 for cyclohexane and p-dioxane mixed solvent and 0.40 for cyclohexane and tetrahydrofuran mixed solvent.

From equation 24, the exciplex emission maxima in mixed solvents of different compositions can then be calculated. The agreement between the calculated values and the experimental values is excellent as shown in Tables VII and VIII.

TABLE VII

Naphthalene-Triethylamine Exciplex Emission Maxima in Cyclohexane and p-Dioxane Mixed Solvents

Mole Fraction of p-Dioxane ($x_{p\text{-dioxane}}$)	$(\bar{\nu}_{Mix})_{expt}$ [a] in cm^{-1}	$(\bar{\nu}_{Mix})_{cal}$ [b] in cm^{-1}	$\Delta\bar{\nu}$ [c] in cm^{-1}
0.00	24401.6	24401.6	0.0
0.12	23826.5	23832.9	- 6.4
0.25	23394.6	23377.1	17.5
0.48	22753.7	22773.9	- 20.2
0.67	22472.9	22401.9	- 71.0
0.85	22174.4	22116.5	57.9
1.00	21932.2	21932.2	0.0

a. Exciplex emission maxima are determined experimentally with reference to the mercury lines.
b. Exciplex emission maxima are calculated from equation 24.
c. Difference of the calculated value from experimental value.

TABLE VIII

Naphthalene-Triethylamine Exciplex Emission Maxima in Cyclohexane and Tetrahydrofuran Mixed Solvents

Mole Fraction of THF (χ_{THF})	$(\tilde{\nu}_{Mix})_{expt}$ [a] in cm^{-1}	$(\tilde{\nu}_{Mix})_{cal}$ [b] in cm^{-1}	$\Delta\tilde{\nu}$ [c] in cm^{-1}
0.00	24408.7	24408.7	0.0
0.29	22899.5	22900.8	- 1.3
0.54	22262.8	22177.4	85.4
0.78	21815.0	21730.3	84.7
0.93	21535.9	21521.1	14.8
1.00	21435.3	21435.3	0.0

a. Exciplex emission maxima are determined experimentally with reference to the mercury lines.
b. Exciplex emission maxima are calculated from equation 24.
c. Difference of the calculated value from experimental value.

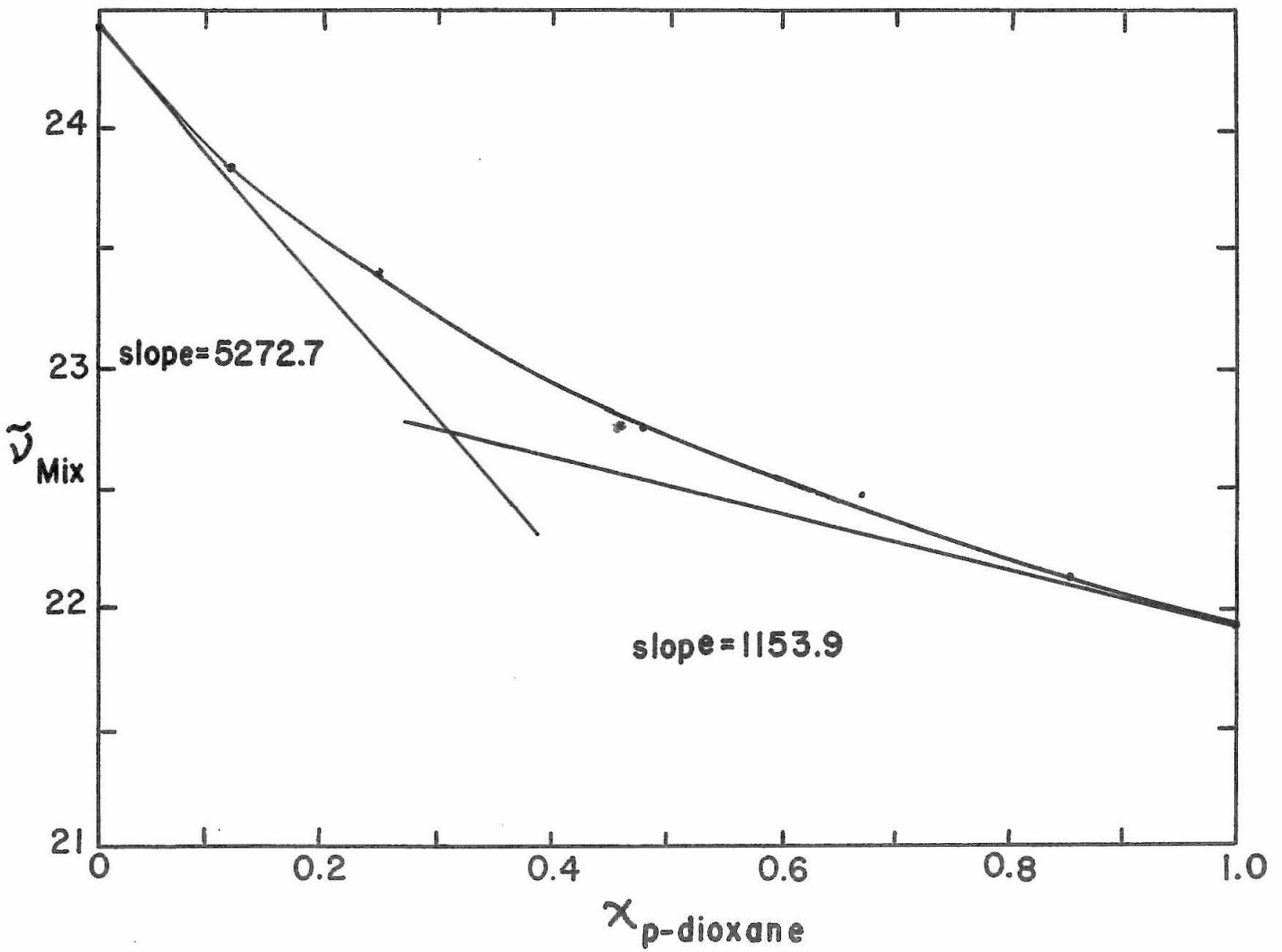


FIGURE XI: Naphthalene-Triethylamine Exciplex Emission Maxima as a Function of Mole Fraction of p-Dioxane in the Mixed Solvents.

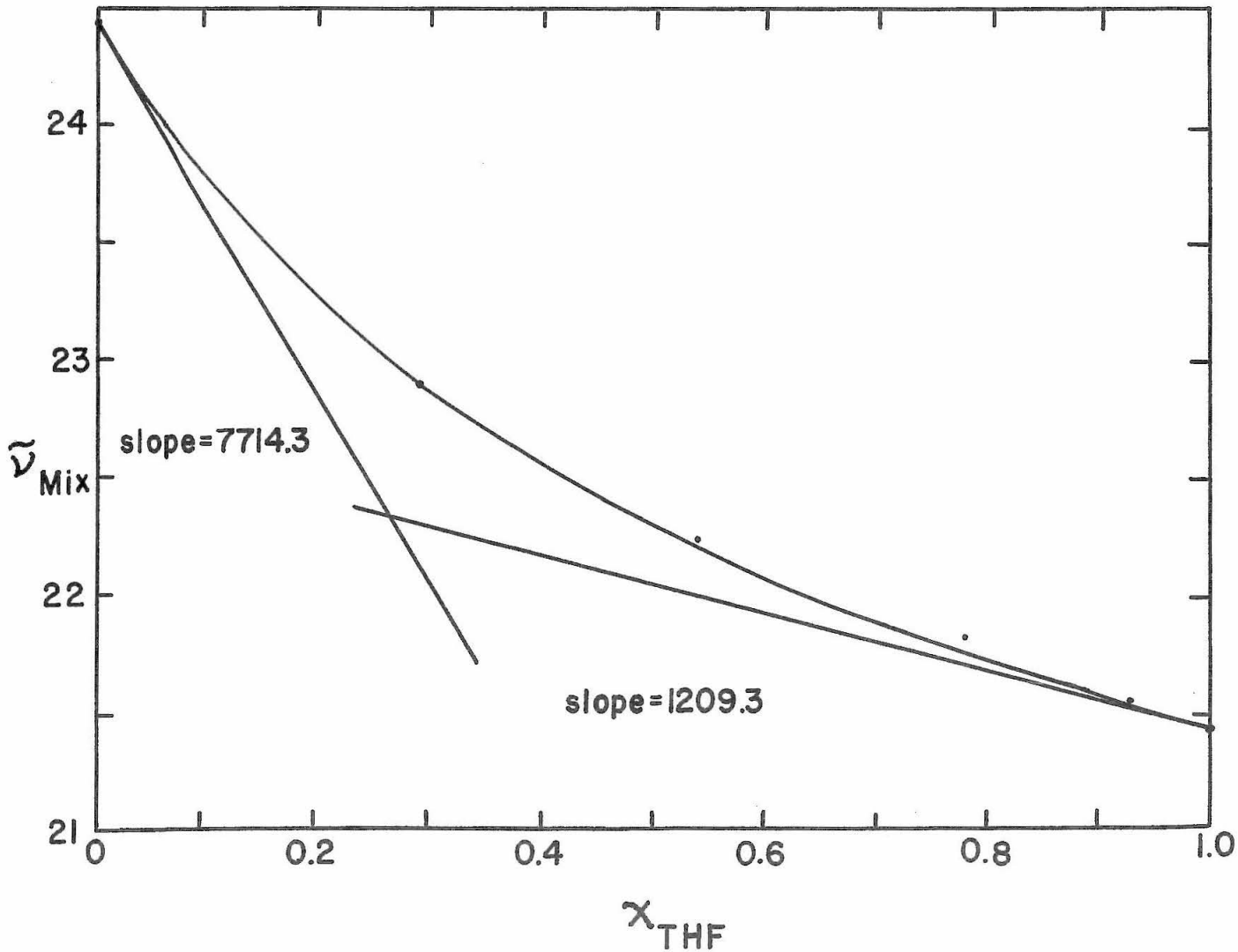


FIGURE XII: Naphthalene-Triethylamine Exciplex Emission Maxima as a Function of Mole Fraction of Tetrahydrofuran in the Mixed Solvents.

EXPERIMENTAL

Amines

Triethylamine (Matheson Coleman & Bell) was refluxed with acetic anhydride for one day and then distilled. The middle portion was then distilled over barium oxide twice and over metallic sodium twice. Each time the middle portion was collected. Purified triethylamine was stored over metallic sodium and was redistilled over metallic sodium just before the preparation of sample solutions, which were degassed immediately.

N-Methylpiperidine was prepared from piperidine (Matheson Coleman & Bell), following H. T. Clark (87). It was then purified in the same way as triethylamine.

Triethylenediamine (DABCO) (Aldrich) was purified by sublimation under vacuum.

Aromatic Hydrocarbons

Benzene (Mallinckrodt, analytical grade) was stirred over concentrated sulfuric acid for several weeks. The acid layer was changed from time to time until it becomes colourless. The benzene was then washed with distilled water, followed with sodium carbonate solution, and distilled water again. After drying with anhydrous magnesium sulfate, the benzene was distilled over phosphorum penta-

oxide once and over metallic sodium twice through the glass-bead packed column (about 1½ meters). Each time middle cut was collected. Purified benzene was stored over fresh metallic sodium.

Toluene (Matheson Coleman & Bell) was purified in the same way as benzene.

Naphthalene (Eastman Organic Chemicals) was recrystallized from reagent grade methanol twice and then further purified by sublimation under vacuum twice.

Fluorene (practical grade) was recrystallized from absolute ethanol six times and further purified by sublimation under vacuum thrice.

Biphenyl (Aldrich, zone refined) was used without further purification.

Carbazole was sublimed twice under vacuum.

N-Methylcarbazole was prepared from carbazole. Metallic sodium (4 grams) in 100 ml p-dioxane was heated to boiling. Carbazole solution (5 grams in 100 ml p-dioxane) was added dropwise through a condense column in about seven hours. Solution was refluxed two more hours and then cooled by ice to about 40° C. The solution was then maintained at 40° C and methyl iodide (about 55 grams) was added dropwise with stirring over a period of 10 hours. After one day, the white precipitate was filtered. The precipitate was

dissolved in ether and chromatographed through an alumina column. The yellowish precipitate was collected after evaporating ether. It was then sublimed under vacuum twice. m.p. 87° C (literature value 88° C)

β-Methylnaphthalene, β-fluoronaphthalene, β-chloronaphthalene and β-naphthonitrile were all purified first by recrystallization from appropriate solvents several times and then by sublimation under vacuum.

α-Methylnaphthalene, α-fluoronaphthalene, and α-chloronaphthalene were all purified by vacuum distillation over $LiAlH_4$ several times. Each time middle cut was collected.

α-Naphthonitrile was recrystallized from n-hexane twice and then sublimed under vacuum once.

Poly-methylnaphthalenes were all used without further purification.

Other aromatic hydrocarbons used in this study were all purified by recrystallization from appropriate solvents, sublimation under vacuum or both.

Solvents

Cyclohexane (Matheson Coleman & Bell) was stirred over a mixture of concentrated sulfuric acid and concentrated nitric acid (5:1) for several hours and then washed with sodium hydroxide solution until aqueous layer was

colourless. Then the cyclohexane was stirred over concentrated sulfuric acid for several weeks. The acid layer was changed frequently and was colourless at the last stage. The cyclohexane was washed with distilled water, followed with sodium carbonate solution, and finally distilled water again. After drying over anhydrous magnesium sulfate, the material was distilled over metallic sodium twice through the glass-bead packed column ($1\frac{1}{2}$ meters), taking the middle cut on both occasions.

n-Hexane and n-heptane were purified in the same way as cyclohexane.

Cyclohexene (reagent grade) was distilled over metallic sodium through a glass-bead column twice. Middle cut was collected each time. The material was distilled over phosphorus pentaoxide through the same column.

1,4-Cyclohexadiene (Aldrich) was used without purification.

Ethyl ether and isopropyl ether were dried over solid potassium hydroxide for one day and then chromatographed through an alumina column (about 1 foot). Distillation over metallic sodium was then followed and the middle portion was collected.

n-Butyl ether and tetrahydrofuran were stored over solid potassium hydroxide for two days. They were refluxed

with $LiAlH_4$ for one day and then distilled. The middle cut was collected.

1,2-Dimethoxyethane (Matheson Coleman & Bell) was refluxed over metallic sodium for one day and then distilled. The middle portion was collected.

1,1-Dichloroethane (Columbia Organic Chemical Co.) was shaken with concentrated sulfuric acid several times until the acid layer was colourless. Then the 1,1-dichloroethane was washed with distilled water several times and dried with phosphorus pentaoxide. The material was distilled over Drierite and the middle cut was collected.

Dichloromethane (Matheson Coleman & Bell) was stirred with concentrated sulfuric acid for one day. It was washed with distilled water twice and then dried over calcium chloride and solid sodium hydroxide for one day. The material was distilled and the middle cut was collected.

Sample Preparation and Apparatus

Fluorescence Studies

Stock solutions of both the aromatic hydrocarbon and quencher (amine) were prepared in cyclohexane (and other solvents). Identical amounts of stock hydrocarbon solution were added to each of several 10 ml volumetric flasks. Measured amounts of quencher stock solution were then added to all but one flask. Samples were then diluted to the mark. About 3 ml of each solution was added to a precision bore pyrex test tube (O.D. = $\frac{1}{2}$ inch) with a constriction about 3 inches from the bottom. These samples were then degassed on a vacuum line (minimum pressure about 10^{-4} mm Hg), using at least three freeze-pump-thaw cycles, and sealed at the constriction.

Fluorescence spectra were taken on an Amico-Bowman Spectrophotofluorometer, maintained at room temperature.

Fluorescence Lifetime Measurements

Samples were prepared in the same way as for fluorescence studies but in quartz tubes.

Fluorescence lifetime was measured by the equipment schematically shown in Figure XIII.

Appropriate emission filters were used in the fluo-

rescence lifetime measurement of aromatic hydrocarbons and their exciplexes.

TRW Model 32A decay time computer can simulate exponential decay. By matching the simulated decay with the observed fluorescence decay on dual beam oscilloscope, fluorescence lifetime can be read on the computer.

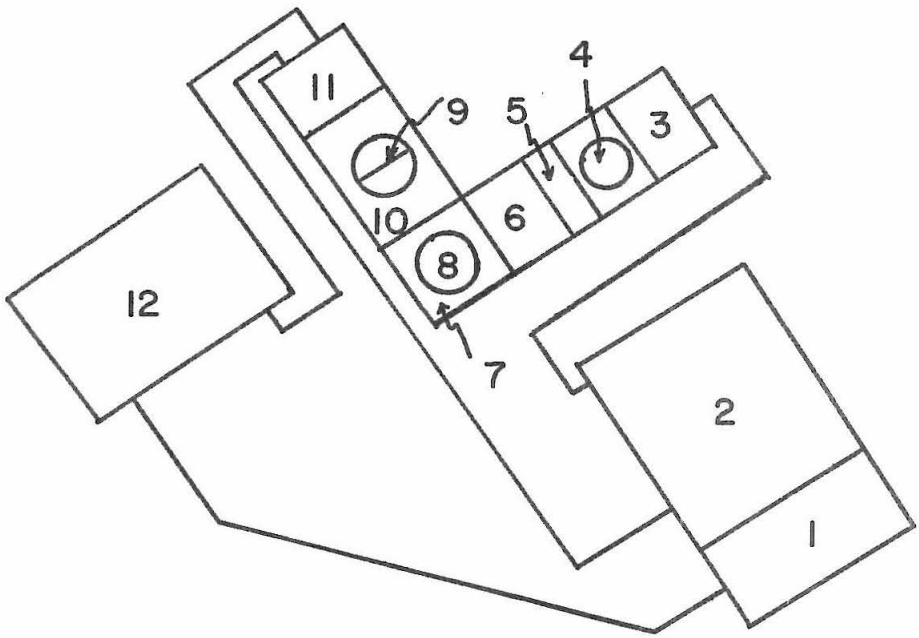


FIGURE XIII: Schematic Diagram of Fluorescence Lifetime Equipment.

1. TRW Model 32A decay time computer.
2. TRW Model 31A nanosecond spectral source.
3. TRW Model 31A nanosecond spectral source (lamp power supply).
4. Deuterium or nitrogen lamp.
5. Filter.
6. TRW Model 38A relay lens assembly.
7. TRW Model 34A fluorescence excitation chamber.
8. Sample.
9. Filter.
10. TRW Model 39A monochrometer.
11. TRW Model 32A photomultiplier.
12. Tektronix Type 556 Dual-beam oscilloscope.

DISCUSSION

Fluorescence Quenching

Fluorescence quenching is defined as any process that results in a decrease in the true fluorescence efficiency of a molecule. Many processes of different natures can result in diverting the excited singlet molecules into decay routes other than fluorescence, causing fluorescence. In this section, several mechanisms leading to the fluorescence quenching will be briefly reviewed (42).

Other than internal conversion and intrinsic inter-system crossing, there are three types of processes that compete with fluorescence, viz., chemical reactions of a molecule in its excited singlet state and non-radiative transfer of excitation energy to an appropriate acceptor by collisional or non-collisional processes.

Chemical Reaction Quenching

The lowest excited singlet state of a molecule has a lifetime of approximately 10^{-8} second, long enough for some competing reactions to take place (43).

Frequently, the chemical nature of the excited singlet state of a molecule is different from that of the ground state. Consequently, excited state reactions are quite often different from those of the same molecule in ground state.

Excited state reactions can be either reversible or irreversible, as ground state reactions are.

The self quenching of the anthracene fluorescence resulting from the photodimerization into dianthracene is one of the examples of irreversible chemical reaction quenching* (4, 5).

Molecules in excited singlet states can also react irreversibly with reactants of other kinds and form stable compounds. The photo-reduction of duroquinone in alcohol solution has been reported to proceed irreversibly through the reaction of the duroquinone in the lowest singlet state with alcohol to form its semiquinone radical (44).

The ionization of molecules in their lowest excited singlet state is a widely used example for this kind reversible chemical fluorescence quenching, e.g., the dissociation of aromatic alcohols and carboxylic acids in their excited singlet states (43, 45-47).

Therefore, chemical quenching is the result of the depopulation of molecules in the lowest excited singlet state through their transformation into some new species,

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*The reversible path is possible when dianthracene absorbs the irradiation energy. However, since its absorption spectrum is different from anthracene's, the reversible path can be prevented by a proper filter system.

which are either non-fluorescent at all or fluorescent at different emission wavelengths.

Non-collisional Energy Transfer (Forster Transfer)

The non-collisional energy transfer is a process that can occur over distance of molecular collision. It must be a truly non-radiative energy transfer process, different from the trivial process of emission of radiation by one molecule and re-absorption of the emitted radiation by another (48). The net result is the transfer of excitation energy from the donor molecule to the acceptor. If the acceptor is fluorescent, the excited acceptor molecules can emit their own characteristic fluorescence, so-called sensitized fluorescence. At the same time, the fluorescence of the sensitizer is reduced.

Non-collisional energy transfer arises from sufficiently large energetic coupling between the sensitizer and the acceptor. The transfer efficiency is favoured by a large overlap of the sensitizer fluorescence spectrum with the acceptor absorption spectrum, long lifetime of the excited singlet state of the sensitizer and large intensity of the transition between the ground state and the excited state of the acceptor. For electric dipole transitions in both molecules, the interaction energy is of a dipole-dipole nature, depending upon the inverse of the third power of

the intermolecular distance. The probability of energy transfer is proportional to the square of this interaction energy. Therefore, it decreases with the sixth power of the distance. It has calculated that this non-collisional energy can occur over distance of 50-100 A (48). Many experimental evidences have shown the validity of this theory (49-52).

Collisional Energy Transfer

As the term implies, collisional quenching is a bimolecular process depending upon "contact" between the excited molecule and the quencher. Several kinds of collisional energy transfer mechanisms will be reviewed here.

Enhancement of intersystem crossing by external heavy-atom effect: It was initially proposed that spin-orbital coupling in a solute is enhanced by quenchers containing heavy atoms, such as alkyl iodides (53). It results in an increasing efficiency of the intersystem crossing of the hydrocarbon and therefore a decreasing efficiency of its fluorescence.

However, now it is generally accepted that this effect arises from the formation of a weak charge transfer complex, in which the fluorescent solute is the electron donor and the halogen-containing species acts as acceptor (54). Through charge transfer mechanisms, the π-electron of the

fluorescent solute may be delocalized over the heavy atom of the quencher. The magnitude of the spin-orbital coupling in the heavy atom then enhances the intersystem crossing probability (54).

Molecular oxygen quenching: Molecular oxygen can quench the excited singlet states, as well as the triplet states, of many compounds, especially aromatic hydrocarbons in solution. Oxygen quenching rates of aromatic hydrocarbons are usually diffusion-controlled, i.e., virtually all collisions between oxygen molecules and hydrocarbon molecules in their lowest excited singlet states are effective (55). Several mechanisms have been proposed to account for the oxygen fluorescence quenching.

In some systems, intermolecular electronic energy transfer from excited solute molecules to oxygen molecules, leading to the formation of excited singlet states of molecular oxygen, has been suggested (56).

Another explanation notes the fact that the ground state of the oxygen molecule is a triplet and therefore paramagnetic. As a paramagnetic species, it increases the spin-orbital coupling of the hydrocarbons, thereby increasing their intersystem crossing rates. This explanation was further confirmed by the fluorescence quenching effect of other paramagnetic species, such as NO (57, 58). The draw-

back of this explanation is shown by its inability to explain the variation of oxygen fluorescence quenching efficiency from one class of fluorescent solutes to another.

Finally, in analogy to the mechanism proposed for the external heavy-atom effect, a charge-transfer mechanism has become popular, with oxygen acting as the electron acceptor (59).

Concentration quenching: It is well known that many substances show appreciable fluorescence only in dilute solutions. With increasing concentration of the fluorescent solute, the fluorescence intensity reaches a maximum and then decreases quite rapidly (60). Two mechanisms have been suggested. One based on the delocalization of the excitation energy and the other on the electron-transfer mechanism.

One special example is the formation of excimer at the high concentration of aromatic hydrocarbons (See INTRODUCTION).

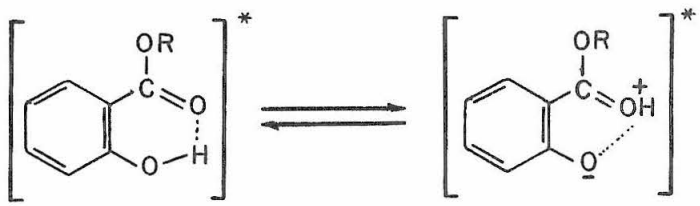
Hydrogen-bonding effect: Hydrogen bonding ability of a molecule may be changed significantly by the photoexcitation. This can cause either red or blue fluorescence shift, depending on the nature of the system (61, 62).

Hydrogen bonding of a fluorescent solute with the solvent (or with another solute) can change the emission

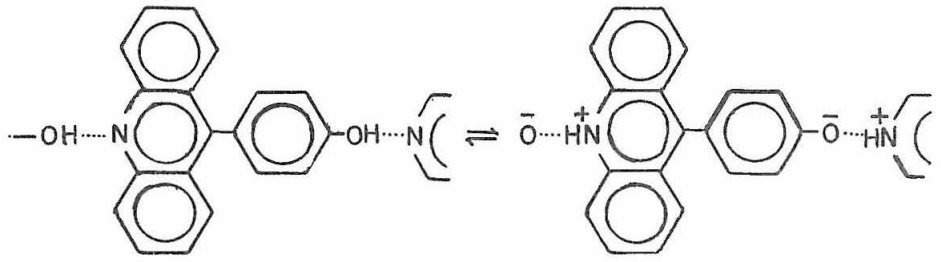
efficiency of the solute.

If the π-electron systems of the donor and acceptor are conjugated via hydrogen bonds, hydrogen bonding quenching can occur by means of the delocalization of π-electrons through these hydrogen bonds. The charge transfer then can be followed by vibronic energy dissipation (63). For instance, fluorescences of both naphthanols and naphthylamines can be quenched by pyridine (63b).

An interesting case of the hydrogen bonding effect on the fluorescence is the proton transfer mechanism, both inter- and intramolecular. The protomeric isomerization of salicylic ester in the excited state results a decrease of the original fluorescence of the ester (43, 64).



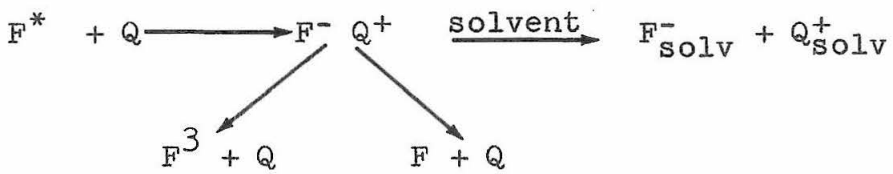
Intermolecular proton transfer is demonstrated by the crystalline 9-oxy-phenyl-acridine (65). Upon long irradiation, the characteristic fluorescence of II is decreased, while the fluorescence intensity characterizing I increases (See next page).



I II

Electron-transfer quenching: Whereas several of the collisional quenching mechanisms discussed above are considered electron-transfer in nature, the actual process of this mechanism is demonstrated by the perylene fluorescence quenching by amines (37, 39).

The processes can be summarized as follows:



The excited fluorescent molecule, F^*, abstracts an electron from the quencher, Q, to form the ion pair $F^- Q^+$. This ion pair can dissociate into a triplet molecule, F^3, and the quencher in the ground state, or simply decay to give ground state of both molecules. Both processes ultimately lead to the dissipation of the excitation energy thermally. In a polar solvent, this ion pair can be solvated to give sepa-

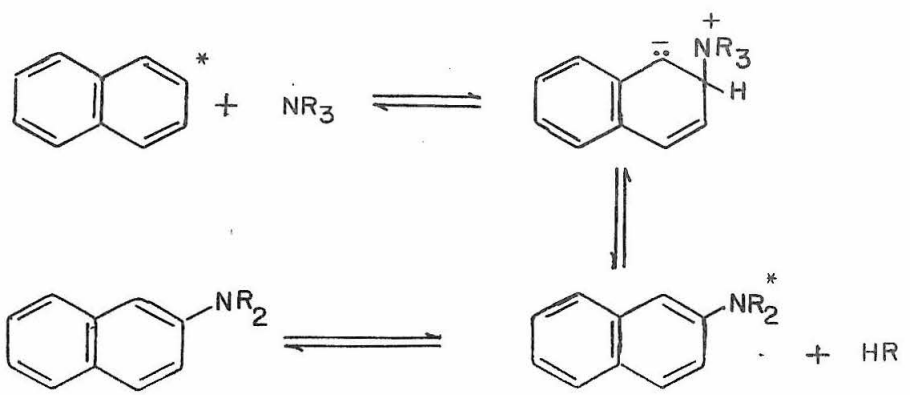
rate ion radicals, F^-_{solv} and Q^+_{solv}. This mechanism is experimentally confirmed by flash photolysis investigations (37c, 39). Furthermore, studies in different solvents indicate that stabilization by solvation of ionic radicals is favoured in polar solvents. In non-polar solvents, additional triplet state population takes place by electron exchange (39).

Experimental evidences also indicate that excited molecules can also serve as electron donors in similar processes (37c).

Anomalous Emissions of Aromatic Hydrocarbons with Tertiary Aliphatic Amine Quenchers

Tertiary aliphatic amines quench the fluorescence of naphthalene and fluorene and simultaneously give an anomalous emission with characteristics similar to the aromatic hydrocarbon excimer emissions. Kinetic studies suggest the mechanism outlined in equations 7-13. However, other possibilities capable of accounting for this anomalous emission have not been eliminated. In this section, these mechanisms and their failure to explain the anomalous emissions are discussed.

Chemical reactions in excited states: If there were any chemical reactions between aliphatic amines and the aromatic hydrocarbon in the lowest excited singlet state, they may be attributed to the increasing electron affinity of the excited hydrocarbon. Therefore, they are more susceptible to nucleophilic substitution than the ground state molecule. The reaction can be visualized as follows:



The anomalous emission is then attributed to the emission of the reaction product. With steady state assumption, relations similar to those of equations 14-16 can be obtained.

If this were really true, prolonged irradiation should change the composition of the solution and result in time dependent emission spectra. This is not observed. Furthermore, no new absorption bands can be observed after irradiation.

Moreover, this result also eliminates the possibility that the anomalous emission arises from the exciplex formed between the excited naphthalene molecules and any N,N-disubstituted naphthylamine (35).

Ion radicals: Similar to the amine quenching of perylene fluorescence (37, 39), tertiary aliphatic amines can quench the hydrocarbon fluorescence through electron-transfer mechanisms, forming the separated ionic radicals of the hydrocarbon and the amine:

$$H^{*} + A \longrightarrow H^{-} + A^{+}.$$

Two possibilities must be considered here. The anomalous emission either arises from the excited hydrocarbon anion radical, or from the recombination of the ion radical pair.

However, it is unlikely that the emission arises from the excited hydrocarbon anion radical. Firstly, there is no vibrational structure in the emission spectrum. Secondly, The difference of the anomalous emission maxima with different amines indicates the participation of the amine in the emission process, naphthalene-triethylamine and -N-methylpiperidine anomalous emission maxima at 409.8 nm and 411.9 nm respectively; and fluorene-triethylamine and -N-methylpiperidine anomalous emission maxima at 385.7 nm and 390.8 nm respectively. Finally, in some polar solvents, such as acetonitrile and ethanol, only fluorescence quenching can be observed, without appearance of a new emission band. Since an ionic radical is more stable in the polar solvent, the absence of the red-shifted emission band gives the support to the rejection of this possibility.

The other possibility is the immediate recombination of the ion radical pairs, emitting photons of longer wavelengths. However, the chemiluminescence from the ion radical recombination would result in the excitation of one of the products of this recombination, with its own characteristic luminescence (66). In these cases, excited product would be the aromatic hydrocarbon with its low-lying excited state. This mechanism seems doubtful. Furthermore, the excited

hydrocarbon will be the same, irregardless of the amine cation involved in the ion radical recombination. The differing emission maxima found with different amines are then hard to explain.

Exciplex: There is but one reasonable explanation remaining: that the anomalous emission arises from an exciplex formed between an excited aromatic hydrocarbon molecule and a tertiary amine molecule. The kinetic study supports this hypothesis, as shown in the result section.

Mechanism of Fluorescence Quenching by Tertiary Aliphatic Amines

The mechanism of the aromatic hydrocarbon fluorescence quenching by tertiary aliphatic amines involves partial electron transfer, resulting in an unstable species, an exciplex, which can accelerate the decay of hydrocarbon molecules in the excited singlet state through both exciplex emission and exciplex non-radiative decay processes. In this quenching process, aromatic hydrocarbon molecules in the lowest excited singlet state serve as electron acceptors and amines as electron donors.

The solvent and substituent effects on the exciplex emission maxima support this view.

The large variation of the exciplex emission maxima with the change of solvents (Table VI) indicates that the exciplex is a very polar species.

An aromatic hydrocarbon molecule in its lowest excited singlet state is not a polar species as shown by the insensitiveness of its emission spectrum to the solvent change. Tertiary amine molecules have small dipole moments (for instance, 0.66 Debye units for triethylamine). Therefore, both individual components of the exciplex are unable to account for such large variation of the emission maxima in different solvents. Consequently, the highly polar exciplex can only result from the redistribution of electron densities of the two components, i.e., partial electron transfer between the two components.

The discussion of the solvent effect on the exciplex emission maxima will be presented in the later section.

The role of the two components in the quenching process can be seen from substituent effects.

If the redistribution of the electron density in the formation of the exciplex decreases electron density on the aromatic hydrocarbon molecule with respect to the free molecule, electron withdrawing groups, such as fluoro-, chloro- and cyano-, on the hydrocarbon molecule will make the exciplex less stable than the unsubstituted one. The higher energy state of the exciplex then should give its exciplex emission maximum at shorter wavelength than the unsubstituted one. This is not the case as shown in Table V.

Therefore, the opposite should be true. The amine serves as an electron donor in the quenching process.

This is further supported by the observation that no exciplex emission is observable when a strong electron donating group such as methoxy is attached to the hydrocarbon molecule (Table V).

Further confirmation can be derived from the quenching of exciplex emission by high concentrations of amines. The exciplex emission intensity increases with the concentration of tertiary amines at first. After reaching a maximum, it decreases with additional increases in the amine concentration. This quenching can be considered to proceed as follows:

$$H^* + A \longrightarrow HA^* \xrightarrow{+A} H^- + (A\ A)^+ \longrightarrow H + A + A.$$

The quenching of exciplex emission by the amine is believed to involve the stabilization of the ion radicals by another amine molecule, followed by either the decay to ground state molecules or the decay to the triplet state of the hydrocarbon through electron exchange. In other words, the quenching of exciplex emission is the result of the amines increasing the non-radiative decays of the exciplex. Similar considerations explain the lack of exciplex emissions in acetonitrile and ethanol solutions. This process is of any

significance only at high concentration of amine.

This effect is further observed in the fluorescence quenching aromatic hydrocarbons by triethylenediamine (DABCO) in cyclohexane solution. The Stern-Volmer relation is observed, with very efficient quenching rates for both naphthalene and fluorene (8.55 and 11.72 $\times 10^9$ M^{-1} sec^{-1} respectively). However, no exciplex emission can be observed at any concentration of DABCO. After quenching the hydrocarbon fluorescence through electron transfer mechanism, the other amine end of DABCO immediately serves as "stabilizer", forming its cation radical. With immediate non-radiative decay, the excitation energy is dissipated.

An anion radical of DABCO would probably be a very high energy species. Consequently, this also supports the idea that tertiary aliphatic amines serve as an electron donor in the quenching of hydrocarbon fluorescence.

Unfortunately, even in the p-dioxane solution, no ion radicals can be observed by esr spectrometry. This may be due to the extremely fast decay of the ion radicals.

Analysis of Exciplex Emission Rate Constants

Table III summarizes the rate parameters obtained in these fluorescence quenching studies by tertiary aliphatic amines. Among them, the exciplex formation rate constant, k_{HA}, its dissociation rate constant, k_{dHA}, and the exciplex emission rate constant, k_{fHA}, are of most interest.

The rate constant of the exciplex formation varies with different hydrocarbons when the quencher is the same, but generally the rates approach the expected diffusion-controlled limit. This indicates that almost every collision between excited hydrocarbon molecules and amine molecules is effective in the formation of exciplex.

The value for β-methylnaphthalene is smaller than the others. Apparently, the steric hindrance due to the methyl group may reduce the effectiveness in the exciplex formation. The steric effect is further shown by the very inefficient quenching of poly-substituted naphthalenes by triethylamine.

Endothermic dissociation of the exciplex can take place at room temperature as shown by the dissociation rate constant. This constant should be sensitive to the temperature.

The most interesting parameter is the emission constant, k_{fHA}. This value should reflect some intimate nature

of the exciplex.

With triethylamine as the quencher, it can be seen that the magnitude of this constant parallels those of the corresponding hydrocarbon's fluorescence transition probabilities, k_{fH}, (β-chloronaphthalene is an exception). A linear relation is observed if k_{fHA} is plotted against k_{fH} (Table III and Figure XIV).

The wavefunction for the exciplex may be written as:

$$\Psi_{HA} \approx \sum_i a_i \phi(H_i^* A) + \sum_j b_j \phi(H A_j^*) + c \phi(H^- A^+) + d \phi(H^+ A^-) \quad (26)$$

where H_i^*'s and A_i^*'s represent various excited states of hydrocarbon H and amine A respectively. Considering the energies, it may be roughly approximately written as

$$\Psi_{HA} \approx a \phi_1(H^* A) + c \phi_2(H^- A^+) \quad (27)$$

where H^* represents the fluorescent state of the hydrocarbon (35).

Let θ_1 and θ_2 be the highest occupied orbital and the lowest vacant orbital of the aromatic hydrocarbon respectively, φ be the n orbital of the amine, the exciplex wavefunction can be represented as:

$$\Psi_{HA} \approx a\underset{\sim}{A}\left|\theta_1 \bar{\theta}_2 \varphi \bar{\varphi}\right| + c\underset{\sim}{A}\left|\theta_1 \bar{\theta}_1 \bar{\theta}_2 \varphi\right|$$

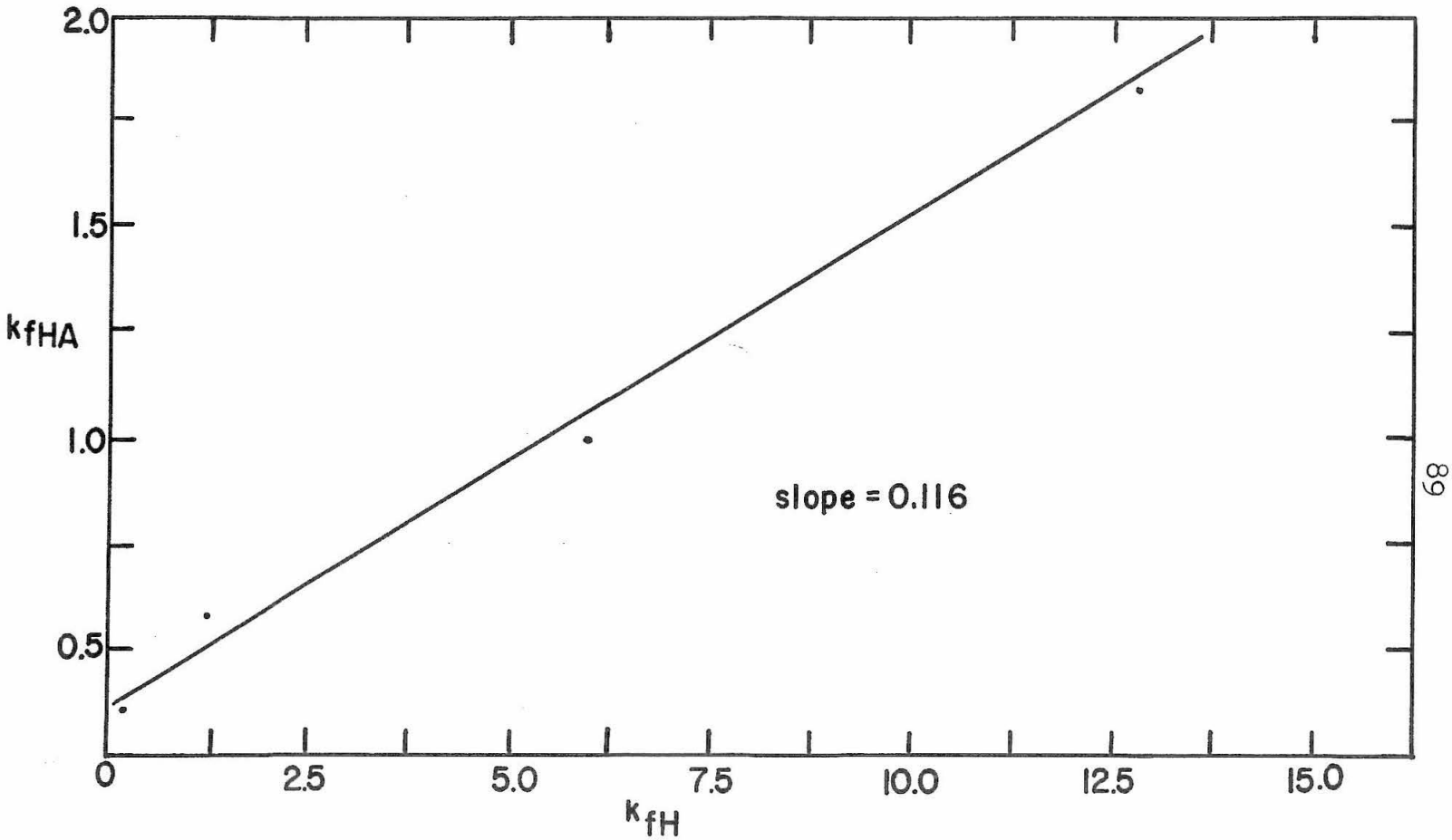


FIGURE XIV: Linear Relationship between Exciplex and Hydrocarbon Transition Probabilities. Both transition probabilities in units of 10^{-7} sec^{-1}.

where $\underset{\sim}{A}$ is the antisymmetrizer operator. The "ground state" of the exciplex can be roughly represented as:

$$\phi_o \ (H\ A) \approx \underset{\sim}{A} \left|\theta_1\ \bar{\theta}_1\ \varphi\ \bar{\varphi}\right|$$

With the assumption that the N atom of the amine sits right above the middle of the aromatic hydrocarbon plane and that the substituents on the N atom can be ignored, the naphthalene-triethylamine exciplex has C_{2v} symmetry. The fluorescent state of naphthalene ($\underset{\sim}{A}|\theta_1\ \bar{\theta}_2|$) has B_{3u} symmetry under the D_{2h} symmetry of naphthalene (67), which becomes B_1 under C_{2v}. The anion of naphthalene ($\underset{\sim}{A}|\theta_1\ \bar{\theta}_1\ \theta_2|$) has B_{2g} symmetry under D_{2h}, which also becomes B_1 under C_{2v}. Therefore, the symmetry of the exciplex wavefunction is B_1, while the "ground state" is A_1.

The transition moment for the exciplex emission can be approximated as:

$$M = e\langle\Psi_{HA}|r|\phi_o\rangle = e\left\{a\langle\phi_1|r|\phi_o\rangle + c\langle\phi_2|r|\phi_o\rangle\right\}.$$

Since only x has the B_1 symmetry in C_{2v}, the transition moment may be simplified:

$$M = e\left\{a\langle\phi_1|x|\phi_o\rangle + c\langle\phi_2|x|\phi_o\rangle\right\}.$$

Transition probability then should be proportional to the square of this transition moment, approximately:

$$e^2\left\{a^2\langle\phi_1|x|\phi_o\rangle^2 + c^2\langle\phi_2|x|\phi_o\rangle^2\right\} .$$

Since the transition moment of the hydrocarbon fluorescence may be approximated as $\langle\phi_1|ex|\phi_o\rangle$, the transition probability of exciplex emission can be expressed as:

$$k_{fHA} \sim C_1\ k_{fH} + C_2\langle\phi_2|ex|\phi_o\rangle^2 \qquad (28)$$

where C_1 and C_2 are proportionality constants. Assuming the substitution on the naphthalene only gives minor perturbation, the same relation should be approximately good for substituted naphthalenes. Following the same analysis, similar relation can be obtained for the fluorene case.

The linear plot between k_{fHA} and k_{fH} (Figure XIV) shows this relation holds. It also indicates the second term of equation 28, i.e., the transition probability arising from the electron-transfer configuration of the excited state to the ground state, gives an almost equal contribution to the exciplex transition.

The exceptional case of β-chloronaphthalene is probably due to that the chlorine substituent gives a perturbation strong enough to make the assumption invalid. Its large exciplex transition probability may arise from other excited states of hydrocarbon through configuration interaction.

In equation 28, C_1 is equal to a^2, which is 0.116 from Figure XIV. Neglecting the overlapping of hydrocarbon orbitals with amine n orbital, the normalization of exciplex wavefunction will give c^2 equal 0.884. Then for naphthalene-triethylamine exciplex, the exciplex wavefunction can be approximated as:

$$\Psi_{HA} \approx 0.34\,\phi_1(H^* A) + 0.94\,\phi_2(H^- A^+). \qquad (29)$$

This exhibits that the wavefunction of the exciplex is mainly that of the electron-transfer configuration. This is consistent with the electron-transfer nature of the exciplex formation process.

General Model of Exciplex Emissions in Solution

Before further discussion of the exciplex emission, a general model is introduced here. Based on the electron-transfer nature of the exciplex, the exciplex formation and its emission can be described by the following steps.

$$H_{(g)} + e \longrightarrow H^-_{(g)} + EA \qquad (I)$$

$$A_{(g)} \longrightarrow A^+_{(g)} + e - IP \qquad (II)$$

$$H^-_{(g)} + A^+_{(g)} \longrightarrow (H^- \cdots\cdots A^+)_{(g)} + e^2/r \qquad (III)$$

$$(H^- \cdots\cdots A^+)_{(g)} \longrightarrow (HA^*)_{(g)} + CBE \qquad (IV)$$

$$(HA^*)_{(g)} \longrightarrow (HA^*)_{(s)} + S_1 \qquad (V)$$

$$(HA^*)_{(s)} \longrightarrow (HA)_{(s)} + h\nu_{HA} \qquad (VI)$$

$$(HA)_{(s)} \longrightarrow H_{(s)} + A_{(s)} + PSE \qquad (VII)$$

$$H_{(g)} \longrightarrow H_{(s)} + S_2 \qquad (VIII)$$

$$A_{(g)} \longrightarrow A_{(s)} + S_3 \qquad (IX)$$

I. The hydrocarbon anion radical is formed in the gas phase by the addition of an electron, with the release of the electron affinity of the hydrocarbon, EA.

II. The amine cation radical is formed in the gas phase by the ionization of the molecule, with the absorption of

the ionization potential of the amine, IP.

III. The ion radical pair is formed in the gas phase by the approach of the two ion radicals, with the release of the electrostatic potential energy e^2/r, where r is the distance between two radical ions.

IV. The exciplex is formed in the gas phase by intermolecular orbital overlapping of the two radicals, with the release of the "chemical bonding energy", CBE.

V. This hypothetical exciplex in the gas phase then dissolves in the solvent, with the release of the solvation energy, S_1.

VI. The exciplex in solution emits a photon $h\nu_{HA}$ and reaches its Franck-Condon ground state.

VII. The Franck-Condon ground state of the exciplex in solution establishes equilibrium with its environment.

VIII & IX. The unexcited hydrocarbon and uncomplexed amine molecules solvate, with release of their respective solvation energies S_2 and S_3.

Steps I and II are straightforward. Only the pure Coulombic interaction is considered in step III, the formation of the ion pair. In step IV, the exchange force between two ion radicals is attributed to the overlapping of the intermolecular orbitals, i.e., the stabilization energy arising from $a\Phi_1(H^* A)$ term of equation 29. Therefore,

this is considered a ""pseudo-chemical bond" (69). In the solvation of the exciplex, step V, the exciplex can be considered a single species with its own physical characteristics, such as a dipole moment. The Franck-Condon ground state of the exciplex, which is reached after the emission of a photon $h\nu_{HA}$, step VI, is of higher energy than the equilibrium state because of the packing strain imposed by the solvent cage, step VII. The solvation of the hydrocarbon and the amine are obviously dependent on both the hydrocarbon and the amine, and also the solvent.

Further discussion of the packing strain energy will be presented in a later section.

By proper addition and substraction of all these equations, the exciplex emission frequency can be expressed as follows:

$$h\nu_{HA} = IP - EA - (e^2/r + CBE) - (S_2 + S_3) - S_1 - PSE \quad (30)$$

This equation is quite similar to Weller's equation for the exciplex emission (37), but with explicit stress on the importance of the exchange interaction of the ion radicals and on the role of the solvent in the formation of exciplex.

Equation 30, derived from the model, will be shown to be very useful in the interpretation of the exciplex

emission phenomenon.

The actual steps in the formation of the exciplex are totally different from the ones shown in the equations. The exciplex is formed when the distance between the excited hydrocarbon molecule and amine molecule eventually becomes small enough that the mutual interaction can occur. This results in the formation of the exciplex with the release of the change of enthalpy of the formation of the exciplex, ΔH. This process is shown by the upper curve of Figure XV.

In this figure, a schematic diagram of the relative energy levels of the exciplex and its ground state is presented as a function of the distance of amine molecule from the aromatic hydrocarbon molecule.

From this figure, the relation between the emission frequency of the hydrocarbon and that of its exciplex can be obtained:

$$h\nu_{H} = -\Delta H + h\nu_{HA} + PSE. \qquad (31)$$

This is exactly the same as the equation derived for aromatic hydrocarbon excimers (15).

Substituting equation 30 into equation 31, the enthalpy change in the formation of the exciplex, ΔH, can be expressed as follows:

$$\Delta H = IP - EA - h\nu_H - (e^2/r + CBE) - S_1 - (S_2 + S_3)$$

$$= IP - EA^* - (e^2/r + CBE) - S_1 - (S_2 + S_3) \qquad (32)$$

where EA^* is the electron affinity of the hydrocarbon in its excited state, which is approximately equal to $EA + h\nu_H$ (70).

From this equation, it is obvious that the formation of the exciplex is favoured by a low ionization potential of the amine, a high electron affinity of the hydrocarbon in its fluorescent state, a large Coulombic and exchange interaction, and large solvation energies.

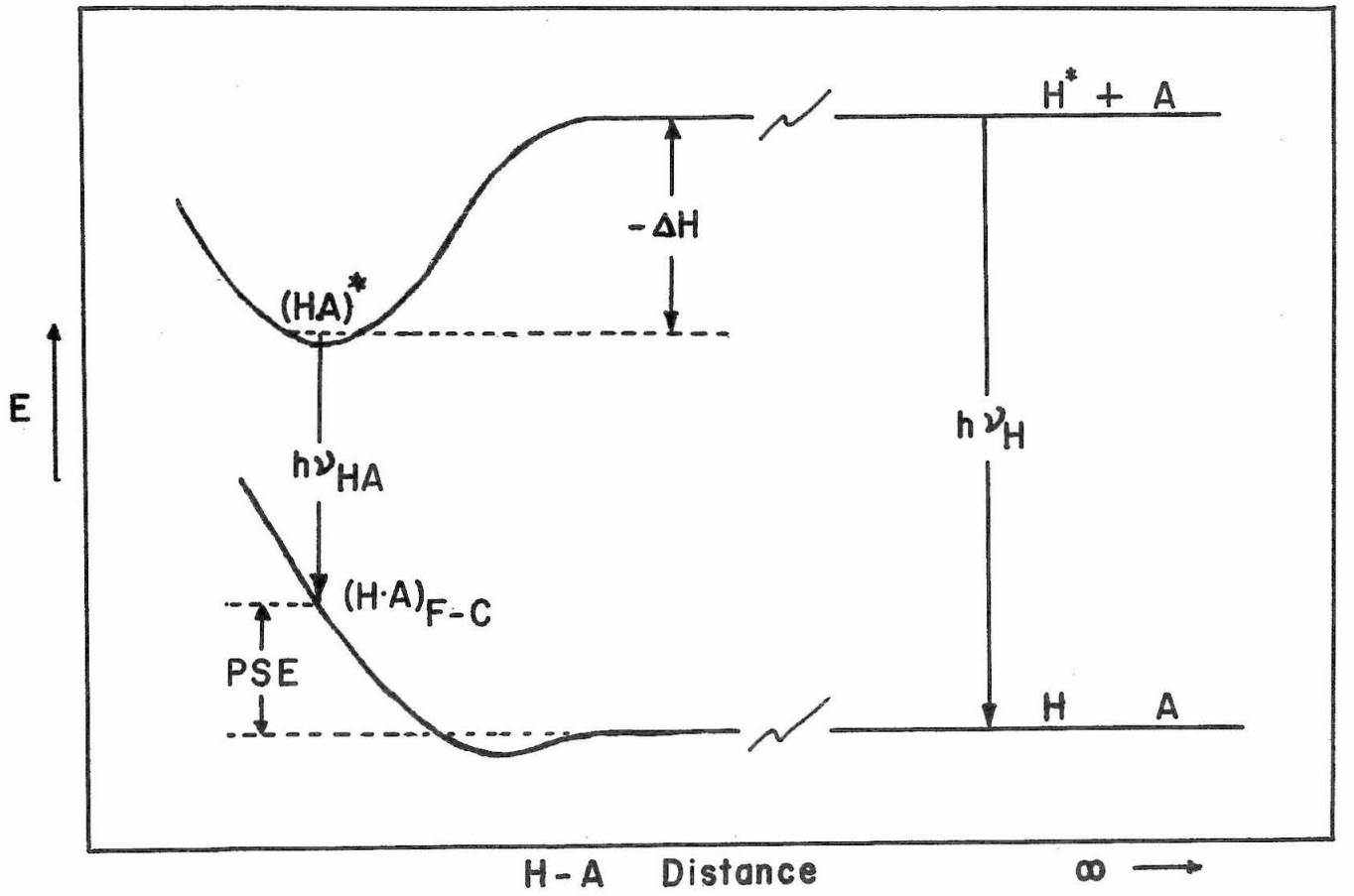


FIGURE XV: Schematic Diagram of Relative Energy Levels of Exciplex and Its Ground State.

Substituent Effect on Exciplex Emission Frequencies in Solution

There are three ways in which a substituent group on the aromatic hydrocarbon can change its exciplex emission frequency. In the first case, substituent groups possessing π-electrons can conjugate with the π-electrons of aromatic hydrocarbons. This is commonly known as mesomeric effect. Secondly, the potential acting on the π-electrons of aromatic hydrocarbons can be modified by substituents. This is so-called inductive effect. Both of these effects can change electron affinities of aromatic hydrocarbons and consequently their corresponding exciplex emission frequencies with the same quencher (equation 30). Finally, steric effects may change the distances between the two partners of exciplexes and thereby change their mutual interactions (72, 73).

Table IX lists the exciplex emission frequencies for substituted naphthalenes with triethylamine as the quencher in cyclohexane solutions (extracted from Table V).

For all these mono-substituted naphthalenes, the steric hindrance cannot vary greatly. Approximately same distances between the components of these exciplexes can be expected. Consequently, we can assume that nearly equal Coulombic and exchange interactions contribute to these exciplex systems. Therefore, in the same solvent, all terms

TABLE IX

Emission Frequencies of Substituted Naphthalene-Triethylamine Exciplexes in Cyclohexane Solution

Substituent	σ^*	α-Substituted Naphthalene-Triethylamine Exciplex Emission Maximum		β-Substituted Naphthalene-Triethylamine Exciplex Emission Maximum	
		in nm	in cm^{-1}	in nm	in cm^{-1}
Methyl-	- 0.17	406.1	24623.9	407.6	24533.9
H-	0.0	409.9	24398.6	409.9	24398.6
Fluoro-	0.062	417.5	23954.4	416.9	23984.4
Chloro-	0.227	432.6	23120.3	425.0	23527.2
Cyano-	0.660	477.4	20946.8	456.8	21889.5

* From Jaffe, Chem. Rev., 53, 222 (1953).

in equation 30 except the electron affinities of the aromatic hydrocarbons are approximately the same. Thus, the change of exciplex emission frequencies upon substitution is attributed to the electron affinity change of aromatic hydrocarbons by the substituents.

The increase of aromatic hydrocarbon's electron affinity by electron-withdrawing groups, such as fluoro- and cyano-, should result in a decrease of exciplex emission frequency. Electron-donating groups, such as methyl-, will give the opposite effect.

These speculations are consistent with the conclusion that the exciplex excited state is mainly of electron-transfer configuration (from the rate parameter analysis). The naphthalene portion in the exciplex has more electron density than free naphthalene. Thus clearly, electron-withdrawing groups on the naphthalene portion will stabilize the exciplex excited state and thereby give emission of lower frequencies than the unsubstituted naphthalene-triethylamine exciplex. Electron-donating groups, such as methyl, will destabilize the exciplex excited state and therefore give exciplex emission of higher frequencies.

Moreover, Hammett's σ values of substituents have been regarded as a measure of the influence of substituents on the electron densities of the carbon atoms when they are

attached to the aromatic hydrocarbons. From the above discussion, the exciplex excited state is more stabilized by a substituent of larger σ value. In fact, electron affinities of substituted aromatic hydrocarbons are linearly related to the σ values of the substituents (74). Therefore, a linear relationship between the exciplex emission frequencies and the σ values of the substituents holds (Figure XVI).

Both Table IX and Figure XVI indicate that exciplex fluorescence frequencies of these substituted naphthalene-triethylamine exciplexes not only depend upon the nature of substituents but also upon their position in the naphthalene molecule. Exciplex emission frequencies of α-substituted naphthalene-triethylamine exciplexes are more affected by substituents than those of their corresponding β-substituted naphthalene-triethylamine exciplexes. That is, for the same electron-withdrawing group, the fluorescence frequency of α-substituted naphthalene-triethylamine exciplex is lower than that of β-substituted one. The opposite is observed for the electron-donating methyl group.

Due to the nature of the approximate wavefunctions involved, the α-carbon atoms bear more of the high electron dnesity of the naphthalene portion of the exciplex than β-carbon atoms, as in the case of the naphthalene anion radical (76). Therefore, it is not surprising that α-substi-

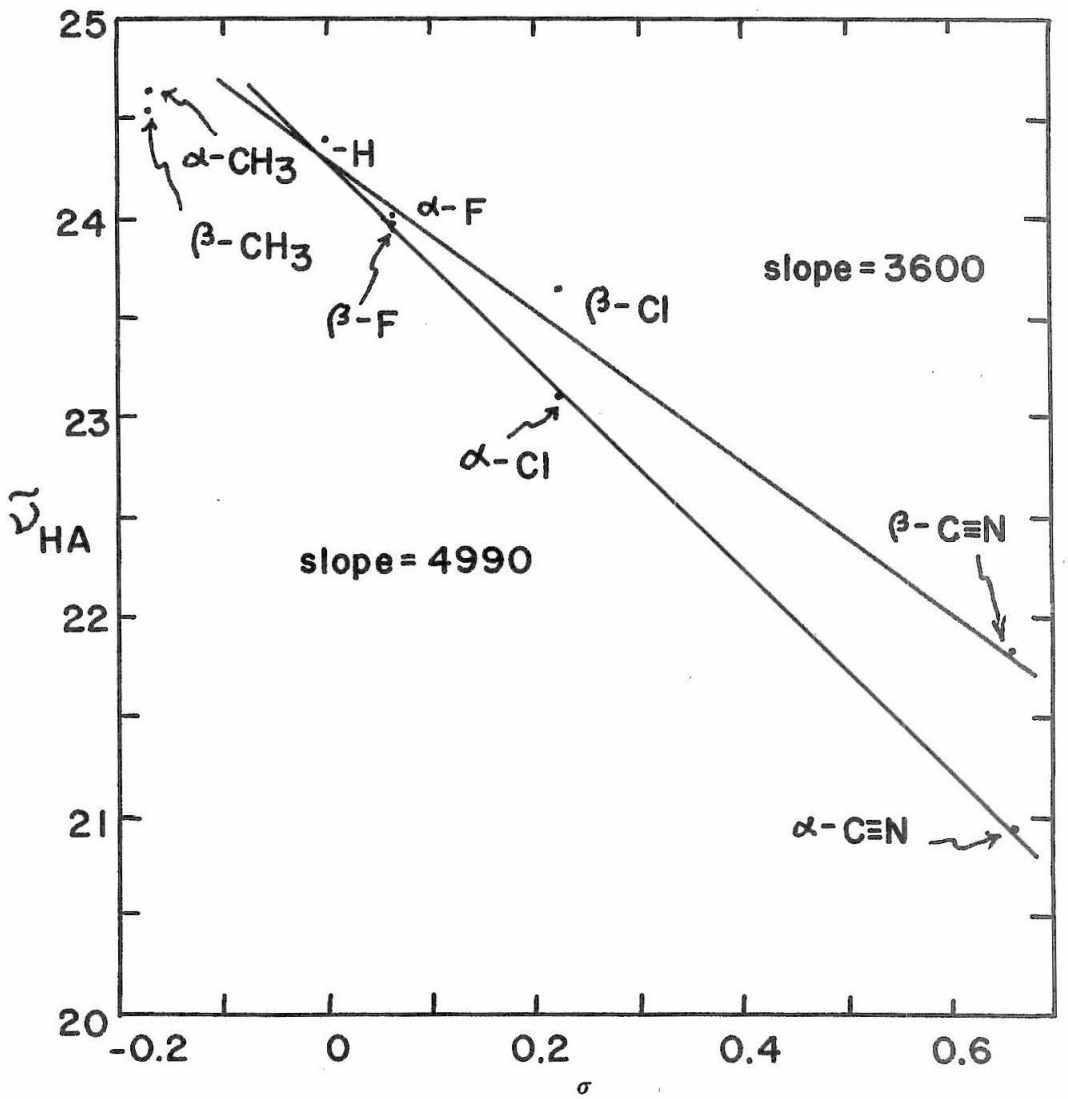


FIGURE XVI: Relationship between Emission Frequencies of Substituted Naphthalene-Triethylamine Exciplexes and σ Values of Substituents. Emission frequencies in units of 1000 cm^{-1}.

tuted exciplex emission frequencies are more susceptible to the substituents than the β-substituted exciplex emission frequencies.

If the exciplex excited state were composed of only the electron-transfer configuration with no intermolecular orbital overlapping, the ratio of the electron density on the α-carbon atoms to that on the β-carbon atoms would be ~2.64 (75-76). However, the influence of α-substituents on exciplex fluorescence frequencies is only ~1.39 times that on β-substituents, i.e., the ratio of two slopes in Figure XVI. This ratio is much smaller than that expected from a purely electron-transfer complex.

This observation is consistent with our model. That is, there actually is intermolecular orbital overlapping, that decreases the electron densities on all of the carbon atoms of the naphthalene anion radical. Yet, the N atom of the amine sits over the center of naphthalene skeleton, and is closer to the α-carbon atoms than to the β-carbon atoms. This geometry reduces the electron densities on the α-carbon atoms more than those on the β-carbon atoms. The ratio of substituent effect on these two different kinds of carbon atoms is thereby reduced from the non-overlapping case.

The steric effects of substituents on naphthalene

is shown by di- and tri-methylnaphthalene-triethylamine exciplex fluorescence maxima (Table V).

With more than two methyl substituents on the naphthalene, the hydrocarbons' own characteristic fluorescences can be observed even in pure triethylamine. The decrease of quenching efficiencies may be not only due to the steric hindrance of the subsituents but also their increased electron-donating nature.

To minimize variations in the solvent effect, the exciplex fluorescence maxima in pure triethylamine are used for comparison.

Some qualitative aspects of the influence of the distance between the two partners of exciplexes can be seen. For example, the emission maxima of the 2,3- and 2,6-dimethylnaphthalene-triethylamine exciplexes differ noticeably from that of the 2,7-isomer. The mesomeric and inductive substituent effects are approximately the same for each exciplex. However, molecular models indicate that the 2,3- and 2,6-isomers experience greater steric hindrance than the 2,7-isomer. This results in a closer contact between the partners of the 2,7-dimethylnaphthalene-triethylamine exciplex and therefore a greater interaction between them. The chemical bonding energy, CBE, increases while the intermolecular distance, r, decreases. This increases the

(e^2/r + CBE) term of equation 30 and predicts the observed decrease in the frequency for the 2,7-isomer. (An exciplex fluorescence maximum of 420.0 nm for the 2,7-dimethylnaphthalene-triethylamine exciplex versus 415.0 nm for the 2,3- and 2,6-dimethylnaphthalene-triethylamine exciplexes.)

This model can interpret the substituent effect on the exciplex emission frequencies quite satisfactorily.

Solvent Effects on Exciplex Emission Frequencies in Solution

The interaction between a solute molecule and the surrounding solvent molecules may cause an energy change of the entire system. Usually, this energy change for an excited state of the solute is different from that of the ground state of the solute. This difference can shift the transition energy between these two states in solution.

Many theories of the solvent dependence of molecular electronic transitions have been presented (77-82). The theories are all based on the same model and lead to slightly different results. Assumptions common to all these treatments are: (1) there are no specific interactions, such as charge-tranfer complexation and association by hydrogen bonding between solute and solvent molecules; (2) the Onsager model is valid (83); (3) the interaction between the solute and solvent molecules is small enough to be treated as a perturbation.

This section presents a brief discussion of McRae's solvent effect theory and its inadequacies in interpreting the solvent dependence of exciplex fluorescence frequencies.

McRae (82) used the products of state functions for the unperturbed component molecules as the zeroth-order electronic state functions of the system. The classical dipole-dipole interaction energy was used as the only inter-

action energy between solute and solvent molecules. By application of perturbation theory to the second order, a general expression for frequency shift was derived. If the Onsager model is used this can be given in terms of macroscopic solvent properties. The emission frequency shift is approximated as:

$$\tilde{\nu}_{(solv)} - \tilde{\nu}_{(gas)} = (A\ L_o + B)\ \frac{n_D^2 - 1}{2\ n_D^2 + 1} + C\left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right]$$

where L_o is the weighted mean wavelength, a characteristic of the solvent; n_D and ϵ are the refractive index and dielectric constant of the solvent; A, B and C are characteristic constants of the solute. In this equation, the interaction between permanent dipoles of solvent molecules and solvent induced dipoles has been neglected. The first term of the equation accounts for the frequency shift due to the dispersion interaction and the interaction between solute permanent dipoles and the induced solvent dipoles. The second term takes care of the interaction between permanent dipoles of solute and solvent.

According to this equation, the plots of exciplex

emission wave numbers $\bar{\nu}_{(solv)}$ against $(n_D^2 - 1)/(2\ n_D^2 + 1)$ should be straight lines for saturated and unsaturated hydrocarbon solvents with no or negligibly small permanent dipole moments. Figures XVII and XVIII show this is true for both naphthalene-triethylamine and fluorene-triethylamine exciplexes[1].

However, the difference of the slopes for saturated and unsaturated hydrocarbon solvents is so large that the difference of the weighted mean wavelengths, L_o, cannot be the only cause of the discrepancy[2]. Moreover, values in ether and chlorohydrocarbon solvents are scattered. At first sight, this seems to be the result of neglecting the dipole-dipole interaction term. However, even with correction for this term, the random pattern is still observed[3]. Therefore, this theory does not interpret the solvent dependence of exciplex fluorescence frequencies satisfactorily.

Since other theories have the same bases as McRae's,

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1 Data are in Table VI.

2 L_o is $\approx$ 1000 A for cyclohexane and saturated hydrocarbons and $\approx$ 1250 A for benzene (82).

3 Taking $L_o \approx$ 1125 A for ethers and chlorohydrocarbons, the plot of $\left\{\nu_{(solv)} - (A\ L_o + B)(n_D^2 - 1)/(2\ n_D^2 + 1)\right\}$ versus $\left\{\{(\epsilon - 1)/(\epsilon + 2)\} - \{(n_D^2 - 1)/(n_D^2 + 2)\}\right\}$ still gives random pattern.

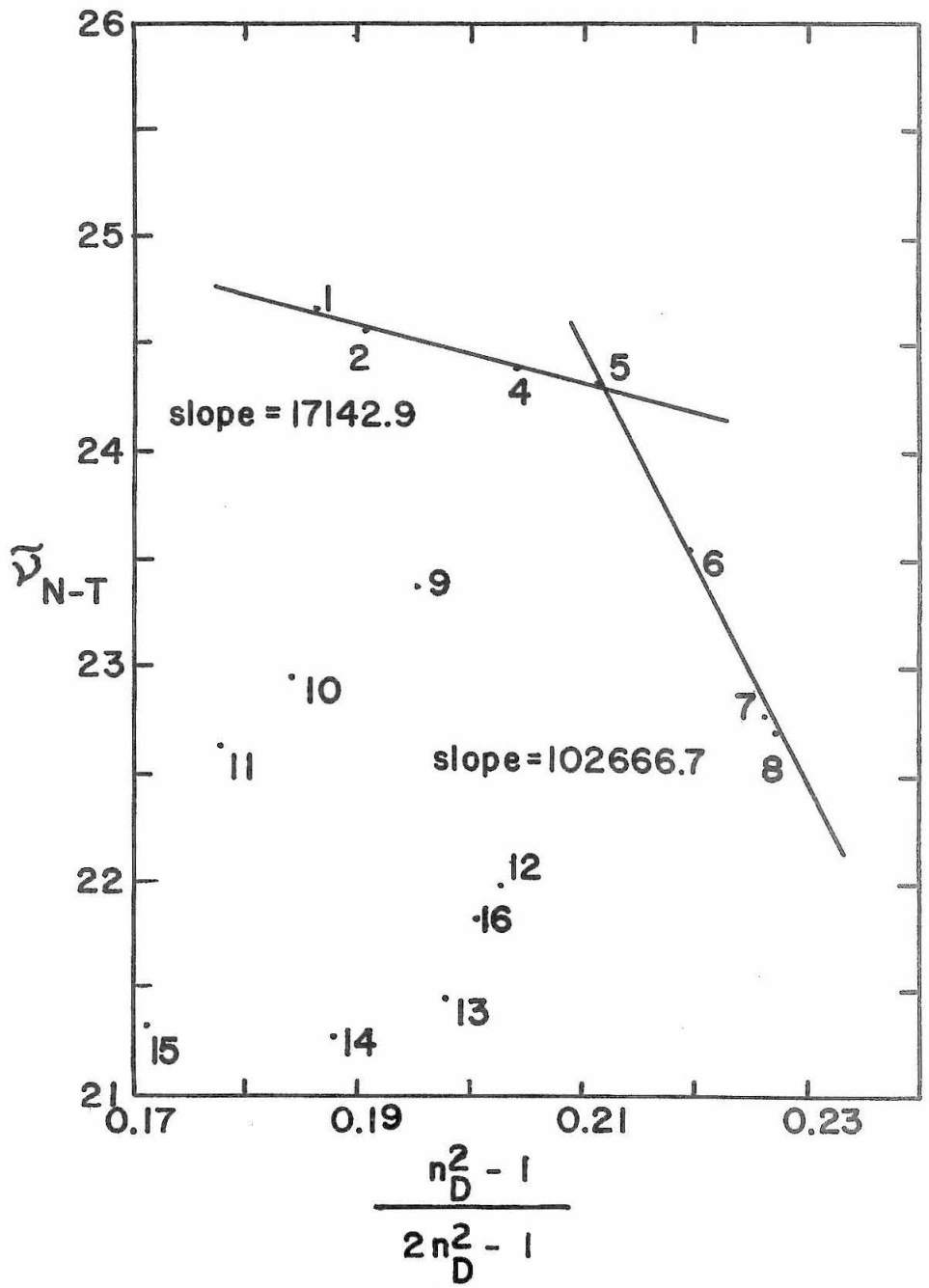

FIGURE XVII: McRae's Treatment of Solvent Dependence of Naphthalene-Triethylamine Exciplex Emission. Emission frequency in units of 1000 cm^{-1}.

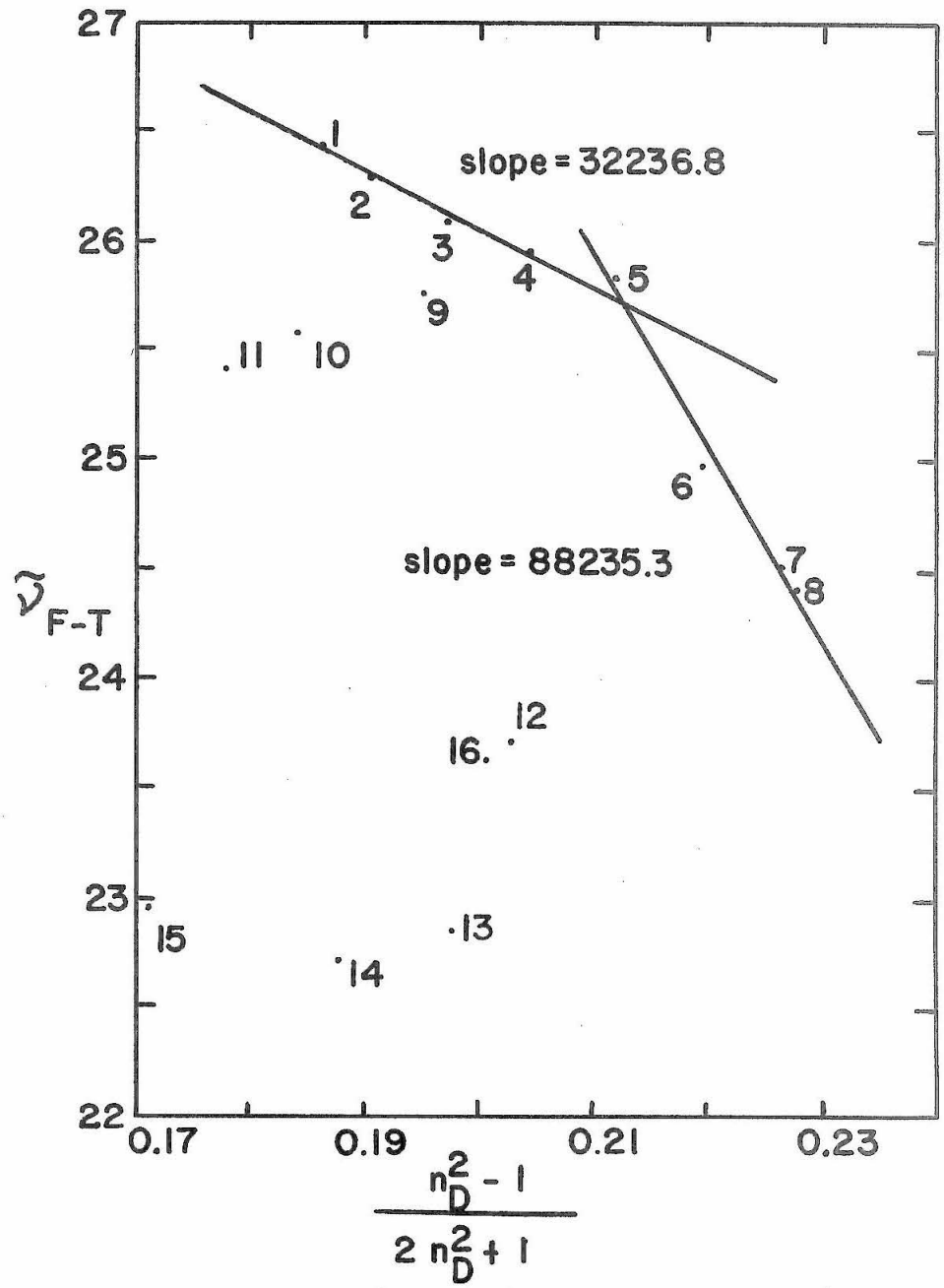

FIGURE XVIII: McRae's Treatment of Solvent Dependence of Fluorene-Triethylamine Exciplex Emission. Emission frequency in units of 1000 cm^{-1}.

the failure of McRae's theory can mean the failure of all others.

The failure is not unexpected for the following reason. All these theories used the assumption that the solute molecule in both states has the same geometry and size. This may be approximately true for most cases but not in the exciplex emission case. In the formation of exciplex from excited aromatic hydrocarbon molecules and tertiary aliphatic amine molecules, the chemical association makes the volume of exciplex smaller than the volume sum of two uncomplexed components. The Franck-Condon ground state of the exciplex should have the same volume as its excited state. The repulsive nature of these two ground state partners plus the packing strain imposed by the solvent make this Franck-Condon ground state of exciplex higher in energy than its equilibrium state. This can be visualized as the energy necessary for the expansion of a volume against an internal pressure imposed by a solvent cage. This is so-called "packing strain energy" in our model.

This term should be a function of properties of both solute (exciplex) and the solvent. Generally speaking, the more polar or more polarizable the solvent, the larger the internal pressure will be. Therefore, ether solvents should give larger packing strain energies than unsaturated

hydrocarbons, which give, in turn, larger strain energies than saturated hydrocarbons.

Therefore, the larger red shift from free hydrocarbon emissions of the exciplex emissions in the polar solvents is the combined result of larger stabilization of its exciplex excited state and larger destabilization of its Franck-Condon ground state.

This packing strain energy term is hard to predict, especially with no way of knowing the volume change during the formation of the exciplexes. However, we can reasonably assume that exciplexes with stronger chemical association will have a larger volume change in their formations, and, consequently, larger packing strain energies in the same solvent.

Estimation of Dipole Moment of Naphthalene-Triethylamine Exciplex

Because of the weak interactions among the non-polar saturated hydrocarbon molecules, we assume that in all saturated hydrocarbon solvents, the packing strain energy is the same for the naphthalene-triethylamine exciplex. Therefore, the change of the exciplex frequencies in these solvents can be approximated by the McRae's solvent theory. Furthermore, we assume that the solvation energy is mainly the interaction energy between the solute dipoles and the induced dipoles of solvent because the solvent is non-polar.

According to McRae (82), the slope of the plot $\tilde{\nu}_{HA}$ vs. $(n_D^2 - 1)/(2\ n_D^2 + 1)$ should be approximately equal to $-\ \mu_{HA}^2/(h\ c\ a^3)$, where h and c have their usual meanings, μ_{HA} is the dipole moment of exciplex and a is the radius of the spherical solvent cavity. Assuming that the radius of the cavity, a, is ~ 3.5 A, the dipole moment of naphthalene-triethylamine exciplex is estimated from the observed slope (17142.9 cm^{-1}, Figure XVII) to be 12.1 Debye units.

The wavefunction of naphthalene-triethylamine exciplex has been estimated in the analysis of rate constants.

$$\Psi_{HA} \approx 0.34\,\phi_1(H^*\ A) + 0.94\,\phi_2(H^-\ A^+). \qquad (29)$$

Therefore, exciplex has 88% nature of electron-transfer

configuration. The distance between two partners in the exciplex is again assumed to be 3.5 A. The dipole moment is then approximately 14.8 Debye units. Considering the crude approxiamtions, the dipole moemnts obtained from these two methods are surprisingly close.

Fluorescence Quenching of Aromatic Hydrocarbons by Primary and Secondary Aliphatic Amines

The fluorescence quenching of aromatic hydrocarbons by primary and secondary aliphatic amines have been observed in cyclohexane solutions. Even though no detailed quantitative data have been collected, two results are obvious:

(1) The fluorescence quenching efficiencies of primary and secondary aliphatic amines are much less than those of tertiary amines.

(2) No exciplex emissions can be observed.

As with tertiary aliphatic amines, the fluorescence quenching occurs by electron transfer from amines to the excited hydrocarbon molecules (37c, 39). Expectedly, primary and secondary aliphatic amines with larger ionization potentials than tertiary amines are less efficient quenchers.

The lack of exciplex emissions with these quenchers can be also attributed to the larger ionization potentials of primary and secondary amines. As shown in equation 32,

the formation of exciplexes is favoured by low ionization potentials of electron donors. The larger ionization potentials of these two amines may not only decrease the change of enthalpy in the formation of exciplexes but also possibly raise energy state of the hypothetical exciplexes above the lowest singlet excited states of their corresponding hydrocarbons (equation 30). These effects may make exciplex emission impossible.

The larger ionization potentials of primary and secondary amines may not be only due to the substituent effects on the N atom of amines but also the association of these amines through hydrogen bonding. This kind of association makes the lone pair electrons of the amine less ionizable.

Alternatively, if the exciplexes are actually formed, even though less effectively, additional non-radiative decay routes are available due to the existence of a breakable N-H bond or to the possibility of intermolecular hydrogen bonding with other amines.

In either case, these factors explain the absence of exciplex emissions with primary and secondary amines as quenchers.

Fluorescence Quenching of Polynuclear Aromatic Hydrocarbons by Triethylamine

Fluorescence of aromatic hydrocarbons with more than two fused benzene rings can be quenched by triethylamine. However, no anomalous emissions can be observed (Table IV).

As in discussion of the last section for primary and secondary aliphatic amines as quenchers, the absence of exciplex emissions with these polynuclear aromatic hydrocarbons as fluorescent substances can be attributed to the unfavorable factors in the formation of exciplexes and/or the fast non-radiative decay processes of any exciplex created.

From equation 32, the change of the enthalpy in the formation of exciplexes increases with the electron affinity of the hydrocarbon molecules in their excited singlet states. The electron affinities of these polynuclear aromatic hydrocarbons in their excited singlet states can be estimated from the sum of electron affinities of the hydrocarbons in their ground states and their transition energies from the excited state under consideration to their ground states (70). For instance, electron affinity of anthracene in its lowest excited singlet state is 3.74 eV and that of naphthalene is 3.56 eV (84). Therefore, the electron affinities of these polynuclear aromatic hydrocarbons in their lowest singlet excited states do not differ

much from that of naphthalene. If electron affinity in the excited singlet state were the only factor influencing the formation of exciplexes, aromatic hydrocarbons with more than two fused benzene rings should be equally or even slightly more likely to form exciplexes with triethylamine.

However, another factor also may be important in the formation of exciplexes. The excited singlet orbitals of polynuclear aromatic hydrocarbons are more spread out than those of small hydrocarbons such as naphthalene. That is, electron densities of the lowest excited singlet orbitals are relatively small in these polynuclear aromatic hydrocarbons in comparison to those of smaller aromatic hydrocarbons. Therefore, the intermolecular orbital overlappings between the lowest excited singlet orbitals of polynuclear aromatic hydrocarbons and the compact n orbital of triethylamine are small. This will affect the formation of exciplexes in two ways, both unfavorable. First of all, small intermolecular orbital overlappings will give small "chemical bonding energy", CBE, term in equation 32. The tendency for the formation of exciplexes is thereby decreased. Secondly, the weak chemical bonding of exciplexes means a small volume change in the formation of exciplexes. This will result a small "packing strain energy" term. From equation 30, small values of PSE term will give high

exciplex emission frequencies. If the frequency of the exciplex emission is comparable to that of the hydrocarbon fluorescence, its observation is unlikely.

Furthermore, it is well known that the anion radicals of polynuclear aromatic hydrocarbons are more stable than those of small hydrocarbons. This may enhance the non-radiative decay processes of exciplexes either through the dissociation to ion radicals in polar solvents, i.e., pure triethylamine, or decay to their triplet states by electron exchange mechanism in non-polar solvents (39). These processes may be fast enough to totally eliminate the possibility of observing exciplex emissions.

Exciplex Emissions in Mixed Solvents

Fluorescence frequencies of naphthalene-triethylamine exciplex change with the composition of mixed solvents (Tables VII and VIII, Figures X and XI). Two mixed solvent systems are used in this study, cyclohexane-p-dioxane and cyclohexane-tetrahydrofuran. In both cases, when a small amount of the polar component (p-dioxane* or tetrahydrofuran) was initially added into a cyclohexane solution, a considerable displacement of the fluorescence frequencies occurred relative to the positions in pure cyclohexane.

The same phenomenon has been reported for fluorescent substances of large dipole moments, such as 4-nitro-4'-dimethylaminostilbene (85).

The analysis of data in the result section indicates that the composition of the solvent in the immediate vicinity of the solute (naphthalene-triethylamine exciplex) differs from that of bulk solution. The polar solvent component is more concentrated around the polar solute molecule than the non-polar cyclohexane.

The excellent agreement between the experimental and

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*Macroscopically, p-dioxane is non-polar.

calculated values in Tables VII and VIII supports this argument. However, the physical meaning of the parameter, the index of preferential solvation, α , is not obvious.

J. Padova applied thermodynamic treatment to the calculation of preferential solvation in mixed solvents. The preferential solvation was interpreted in terms of partial molar free energies of solvation. The index of preferential solvation α is equal to $-(\Delta G_1 - \Delta G_2)/2.3\ RT$, where ΔG_i is the partial molar free energy of solvation in component i of the binary solvent (68).

The difference of exciplex emission frequencies in two components of the mixed solvent was taken as the difference of the free energies of solvation in two solvents. The calculated α values by Padova's method are much larger than experimental values.

T. Yoshino discussed the solvent effects on infrared absorption bands in binary solvents (86). Based on the assumption of binomial distribution of solvent molecules around the solute molecule, his conclusion is that the index of preferential solvation α is equal to $\Delta E/2.3\ nRT$, where ΔE is the difference of solvation energies in the pure components of the mixed solvents, and n is the number of solvent molecules surrounding each solute molecule.

Yoshino's result is different from that of Padova,

due to their different approaches. Padova's thermodynamic treatment considered the solvent as a uniform medium and the composition changes affected the solvent properties as a whole. Yoshino considered the molecular distribution around the solute in a statistical manner. Yoshino's result is therefore used in this treatment of the microscopic environment effects on exciplex emissions in mixed solvents.

Once again, the difference of exciplex emission frequencies in the two components is taken as the difference of solvation energies of the exciplex in the two components.

The ratio of indices of preferential solvation for the two mixed solvent systems (cyclohexane-p-dioxane and cyclohexane-tetrahydrofuran) is 1.219, which is quite close to the ratio of exciplex emission frequency maxima differences in the two pure components of the system (1.206). This shows a directly proportional relationship between the index of preferential solvation and the difference of exciplex emission frequencies in the two pure components.

If n is taken to be 15.5, the calculated a values for cyclohexane-p-dioxane and cyclohexane-tetrahydrofuran mixed solvents are 0.332 and 0.40 respectively. These are very close to experimental values (0.33 and 0.402). This

suggests that about 15 to 16 solvent molecules surround each exciplex. These are not unreasonable numbers.

Yoshino's treatment seems quite satisfactory in the treatment of exciplex emissions in mixed solvents.

Conclusion

The anomalous emissions in the fluorescence quenching of aromatic hydrocarbons by tertiary aliphatic amines have been shown to originate from species formed between aromatic hydrocarbon molecules in their lowest excited singlet states and tertiary amine molecules. They are called exciplexes.

In the studies of solvent and substituent effects on exciplex emission frequencies, the exciplex formation process is concluded to be partially electron-transfer in nature with excited aromatic hydrocarbon molecules serving as electron acceptors and tertiary aliphatic amine molecules as electron donors.

On this basis, a partially electron-transfer model of exciplex was considered. The stability of these exciplexes is attributed not only to the Coulombic interaction between ion radicals but also the exchange force due to the intermolecular orbital overlapping of the ion radicals, designated as the "chemical bonding energy".

Furthermore, the red-shift of the exciplex emissions

from the hydrocarbon fluorescences are due to two factors. Firstly, the excited state of the exciplexes is of lower energy than the lowest excited singlet state of the corresponding hydrocarbons by an amount equal to the change of enthalpy in the formation of exciplexes. Secondly, the Franck-Condon ground state exciplexes are of higher energy than their equilibrium states because of the packing strain imposed by the solvent cage and the change of volume in the exciplex formation.

The quenching of aromatic hydrocarbon fluorescence is the result of the formation of exciplexes. Through the radiative and the non-radiative decay processes of exciplexes, the excited hydrocarbon molecules become involved in decay processes other than their normal ones -- fluorescence, intrinsic intersystem crossing and internal conversion. The processes following the initial exciplex formation are not necessarily electron-transfer in nature. For instance, the dissociation of exciplexes into solvated ion radicals in polar solvents enhances the non-radiative decay processes such that no exciplex emission can be observed.

However, since the reverse of the exciplex formation occurs, the fluorescence quenching of aromatic hydrocarbons by tertiary aliphatic amines depends not only upon the rate of exciplex formation but also upon the rates of secondary processes following the exciplex formation.

From equations 14 and 17, we can derive the following relationship:

$$\frac{\Phi_{fH}^{o}}{\Phi_{fH}} = 1 + \frac{k_{HA}\, C}{(k_{fH} + k_{rH})\ \{1 + k_{dHA}/(k_{fHA} + k_{rHA})\}} . \qquad (33)$$

There are then two limiting cases. If the dissociation rate constant, k_{dHA}, is much larger than the sum of exciplex fluorescence and non-radiative rate constants, $k_{fHA} + k_{rHA}$, equation 33 may be approximated as:

$$\frac{\Phi_{fH}^{o}}{\Phi_{fH}} = 1 + \frac{k_{HA}}{k_{dHA}} \frac{k_{fHA} + k_{rHA}}{k_{fH} + k_{rH}} C = 1 + \frac{k_{q}}{k_{fH} + k_{rH}} C.$$

The fluorescence quenching rate constant of aromatic hydrocarbons, k_q, then depends not only upon the rate constant of the exciplex formation but also upon other rate parameters as shown above.

If the dissociation rate constant is much smaller than the sum of the exciplex fluorescence and non-radiative rate constants. Equation 33 then becomes the simple Stern-Volmer relationship:

$$\frac{\Phi_{fH}^{o}}{\Phi_{fH}} = 1 + \frac{k_{HA}}{k_{fH} + k_{rH}} C.$$

Only in this case, the fluorescence quenching rate of the hydrocarbons by quenchers will depend on the exciplex formation rate constant only.

The details of the exciplex non-radiative decay processes are unknown. Three possibilities exist. One is the dissociation into ion radicals. This is favoured in polar solvents. Another is the catalysed intersystem crossing of aromatic hydrocarbons through electron exchange. The last is the conversion into vibrationally excited ground state molecules. Further studies of the nature of these processes may help to understand the detailed nature of fluorescence quenching.

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Hydrocarbon	EA in eV[a]	$h\nu_H$ in eV[b]	EA* in eV
Naphthalene	- 0.3	3.86	3.56
Biphenyl	- 0.5	4.04	3.54
Anthracene	0.5	3.24	3.74
Phenanthrene	0.1	3.58	3.68
Triphenylene	- 0.05	3.50	3.45
Chrysene	0.3	3.44	3.74
Perylene	0.85	2.82	3.62

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PROPOSITION I

Photochemical method is proposed for the synthesis of aromatic carboxylic acids.

Classical preparation methods of aromatic carboxylic acids are the oxidation of the carbon side chains of the aromatic hydrocarbons and the carbonation of aryl organometallic compounds (1, 2). Both of these methods have some disadvatages.

Oxidation method usually gives a low yield of the desired products due to the destructive nature of the oxidizing agents to the ring systems. Moreover, this method cannot preserve the side chains of aromatic system at all.

In the carbonation method, one of the starting materials is aryl organometallic compounds, which are usually prepared by mixing aromatic hydrocarbons with alkyl organometallic compounds, such as alkyl-lithiums or -potassiums. These organometallic compounds are very reactive and can engage in other kinds of chemical reactions besides carbonation. Consequently, precautious measures must be taken to prevent side reactions in the carbonation process. Furthermore, this method is not applicable when there are

reactive substituents, such as hydroxyl and halogen, on the alkyl side chain of aromatic hydrocarbons.

Molecules of aromatic hydrocarbons in their lowest excited singlet states can be quenched by tertiary aliphatic amines through the formation of exciplexes (3). In polar solvents, these exciplexes are favoured to dissociate to ion radicals. Triethylenediamine (DABCO) is the quencher most favourable for this dissociation process to take place (3). The presence of the aromatic hydrocarbon anions may make the carbonation of the aromatic hydrocarbons possible if carbon dioxide is present in the solution during irradiation.

Along this line of thinking, a premitive experiment has been done.

About 1 gram fluorene and 12 grams DABCO were dissolved in 100 ml p-dioxane. Carbon dioxide gas was bubbled through this solution in a photochemical vessel for 45 minutes. Then it was irradiated by pyrex-filtered Hanovia 450W medium pressure mercury lamp for three days. During this period, carbon dioxide gas was kept bubbling through the solution. After evaporation of the solvent, HCl solution was added to remove DABCO. The residue was then filtered and dried under vacuum. Thin layer chromatography

showed that this residue contained fluorene and an unknown compound whose position is comparable to that of 9-fluorenecarboxylic acid obtained by the metalation and carbonation of the fluorene. The residue was then treated with concentrated sodium hydroxide solution and the undissolved organic compound was removed by filteration. The filtrate was then acidified by concentrated HCl solution. A small amount of precipitate was collected by filteration and dried under vacuum. The melting point of this precipitate is about 213° C (m. p. of 9-fluorenecarboxylic acid is 219-224°). Even though the amount of the precipitate is too small for further purification and identification, it is very likely that this is 9-fluorenecarboxylic acid.

The result of this premitive experiment is quite encouraging.

The low yield is not necessarily due to a low quantum yield of the photochemical reaction. It is more likely due to the low concentration of carbon dioxide in solution and/or the possible decomposition of the carboxylic acid under irradiation.

It is therefore proposed that the same experiment should be done under high pressure of carbon dioxide and in an optimum p-dioxane-water mixture to increase the concentration of carbon dioxide in solution. The mixture may

also increase the ionization of carboxylic acids. Proper filter systems may be used to prevent the possible photodecomposition of the carboxylic acids.

The advantage of this photochemical method is that the side chain of the aromatic hydrocarbons, even those containing active substituents, can be preserved. This is due to the immediate carbonation of the aromatic anions after their formation in the subsequent processes of the fluorescence quenching.

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PROPOSITION II

Application of nuclear quadrupole resonance technique in the study of the adsorption phenomenon is proposed.

The phenomenon of adsorption has been known for years. Basically, two types of adsorption have been observed, i.e., physical adsorption and chemical adsorption (chemisorption). Physical adsorption is known as a process in which the bond between the adsorbent and the adsorbate is of the van der Waals type, and therefore is characterized by a low heat of adsorption. On the other hand, chemical adsorption, which is characterized by a high heat of adsorption, is considered as a process leading to a strong chemical interaction between the adsorbent and the adsorbate (1, 2).

Adsorption phenomenon can occur at all surfaces. Five types of interface exist, i.e., liquid-liquid, liquid-solid, gas-liquid, gas-solid and solid-solid. Among these, gas-solid adsorption has been quite thoroughly investigated (1, 2). Liquid-solid adsorption is receiving attention because of its importance in the biological systems (3).

However, the actual nature of the bond formed between the adsorbent and adsorbate is still an unknown, even though the application of the infrared spectroscopy toward this goal is under way (4). The importance of the detailed knowledge in the basic force leading to the adsorption process makes more thorough investigation desirable.

Nuclear quadrupole resonance spectroscopy has been known as a technique which can detect the change of the electronic configuration around a nucleus possessing a quadrupole moment. The change of the electronic configuration alters the inhomogeneous electric field on the nucleus generated by the charge cloud arount it. This change causes an alternation in the interaction energies between the field and the nuclear quadrupole moment, and consequently, a change in the transition energy in the pure quadrupole resonance frequency (5, 6, 7).

The interaction between the adsorbent and the adsorbate must cause the change of the electronic configuration of the adsorbate in both physical and chemical adsorptions. Therefore, when the active site of the adsorbate contains a nucleus with a quadrupole moment, such as amines $N^{14}R_3$, the difference in the nuclear quadrupole resonance frequency of the adsorbate from that of its free

form in the gas phase will give the information about the change of the electronic configuration of the adsorbate, and consequently some nature of the bonding between the adsorbate and the adsorbent.

Furthermore, this technique may be used to determine the adsorption isotherm directly. In the gas-solid adsorption case with the gas molecules containing a nucleus possessing a quadrupole moment, two different nuclear quadrupole resonance frequencies can be observed, one corresponding to the free gas molecule and the other to the adsorbed molecules. The relative intensities of these two transitions will give the ratio of the molecules in the gas phase to that adsorbed on the adsorbent. The variation of this ratio with the pressure of gas at constant temperature will give a direct determination of the adsorption isotherm for the gas-solid (8).

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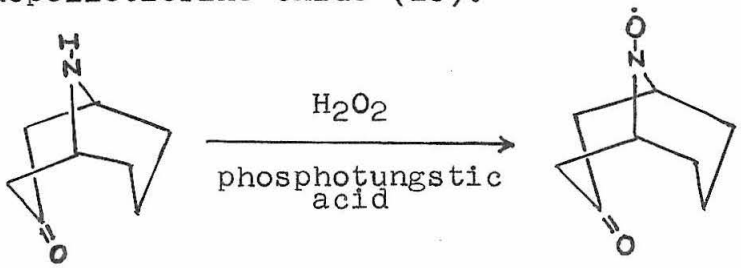
PROPOSITION III

The conformations of the stable nitroxide radicals are proposed to be investigated through EPR and NMR studies at low temperature.

A large number of stable nitroxide radicals have been prepared either by the oxidation of amines or hydroxylamines, or by the reduction of the nitro compounds. The oxidizing agents usually used are hydrogen peroxide in the presence of sodium pertungstate (1-5) and benzoyl peroxide (6). The reduction is usually initiated polarographically (7).

The stability of these radicals is attributed to several factors: (i) The steric inhibition of N-N or N-O bond formation prevents the formation of the dimer, which is considered to be the main stabilizing factor in the case of 2,2,5,5-tetramethylpyrrolidine N-oxide radical and di-t-butyl nitroxide (3-5, 7-9). (ii) The delocalization of the unpaired electron onto the fluorine atoms on the neighboring substituents or onto aromatic rings, which is thought to be responsible for the stability of bis-(trifluoromethyl)-nitroxide and diphenyl nitroxide (9, 10, 15).

(iii) Three electron-bond formation between N and O in the radicals is also considered to be a stabilizing factor (7-11). (iv) Rose-Marie Dupeyre et al reported the synthesis of norpserdopelletierine oxide (10).



This radical was found to be stable in the solid state and in benzene or water solution but unstable in the acid or basic solutions. They suggested that the stability of the nitroxide radical is because no double bond can be formed between nitrogen atom and the adjacent carbons through enolization.

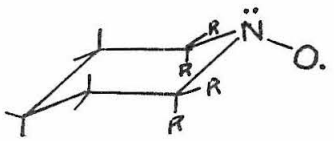
So far, no one has yet studied the conformations of some simple nitroxide radicals, such as alicyclic nitroxide.

Piperidine molecule takes "chair" form as shown by chemical means. The acyl migrationof 1-benzoyl-4-piperidinol takes place at 100° C under the effect of HCl in dioxane but the reversed O to N acyl migration was not observed (16). Furthermore, from the study of anisotropic properties of polarizability of N-H and N-C links, preferential conformations of piperidine and N-methylpiperi-

dine were determined (17). Both of them were confirmed to be in the "chair" form. N-H disposes axially rather than equatorially while the methyl group is attached axially or equatorially with equal probability. Thus it was concluded that the lone electron pair in the ring N-atom has nearly the same size as a methyl group.

Thus there must be a preferential conformation for the substituted piperidine oxide, at least at low temperature. It is proposed that their conformations may be determined from the EPR and NMR studies at low temperature. 2,2,6,6-Tetramethylpiperidine oxide is taken as an example.

Two possible conformations of this radicals are as follows:



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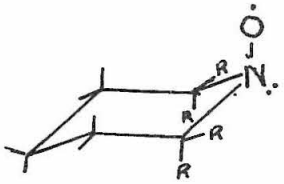

II

If the radical assumes conformation I, the EPR spectrum will consist only three equally spaced narrow lines of equal intensity. These are arised from the hyperfine interaction with nitrogen necleus. No hyperfine structure arises from protons on t-butyl group reported in

the di-t-butyl nitroxide. On the other hand, if the radical assumes conformation II, the two axial protons on 3- and 5-carbons may interact with the free valence and further split the spectrum into three triplets. Each triplet has three lines with intensity ratio 1:2:1.

In the NMR Study of radicals, E. de Boer and C. Mclean observed that the proton resonance lines are shifted in the anion radical in comparison to the neutral compound (18). K. H. Hausser et al (19) pointed out that only those protons having small coupling constant will show the resonance lines. Thus in TBP (2,4,6-tri-t-butyl-phenoxyl) radical, only protons on the two ortho-t-butyl groups (a = 0.072 G) show the proton resonance line while both ring protons (a = 1.67 G) and protons on p-t-butyl group (a = 0.36 G) do not.

Therefore if the radical assumes the conformation I, it will show proton resonance lines for both protons onto the four methyl groups and also those on 3-, 4- and 5-carbons in the ring. However, if it assumes the conformation II, it will only show proton resonance lines of methyl protons and protons on carbon 4 in the ring (probably two equatorial protons on carbon 3 and 5 too). By comparison of line intensities with reference to that

of methyl protons, the information of the conformation may be taken as a supplement to the EPR study.

It may be even more ideal to use 2,2,6,6-tetrachloropiperidine oxide. The EPR analysis will be the same. In the NMR study, a comparison of the intensities may be made with piperidine proton resonance.

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PROPOSITION IV

Intramolecular triplet energy transfer in the compounds with fixed conformations are proposed.

The intramolecular electronic energy transfer between two non-conjugated chromophores has been investigated in the past few years. Most works were concerned with the singlet excitation energy transfer in the solution at room temperature or in the rigid glass at liquid nitrogen temperature (1, 2). D. S. McClure (3) observed the singlet energy transfer in the "double molecule", such as biphenyl, in the crystal form.

Hammond et al (4) reported the intramolecular triplet excitation energy transfer between the benzophenone moiety and naphthalene moiety, which were connected with different number of methylene groups. With the excitation light which only benzophenone moiety absorbed, only naphthalene phosphorescence could be observed.

It is suggested that in certain systems, which will be discussed later, the exciton interaction is responsible for the intramolecular triplet energy transfer and the direct measurement of this interaction may be made with the method of variation of energy denominator developped by Robinson et al (5).

In the survey of energy transfer in the mixed benzene crystal of C_6H_6 in C_6D_6, $C_6H_3D_3$ and $C_6H_4D_2$(6, 7), and also in the mixed naphthalene crystal of $C_{10}H_8$ in $C_{10}D_8$ (8), long range triplet energy transfer was observed. Robinson et al pointed out that "the degree of triplet energy transfer per triplet lifetime to be substantially greater than the degree of singlet energy transfer per singlet lifetime". By doping C_6D_6, $C_6H_3D_3$ and $C_6H_4D_2$ respectively with C_6H_6 and observing the energy shifts of the lowest triplet state of benzene through the phosphorescence study, the nearest neighbor pair interaction matrix element can be obtained with the formula

$$\delta = 4\beta^2 \Delta E^{-1}$$

where δ is the energy shift observed in the phosphorescence, β is the interaction matrix element, and ΔE is the energy difference in the triplet states of the host and the guest molecules.

A series of compounds, diphenylcyclopentanes, may be used for the measurement of this interaction matrix element in the intramolecular energy transfer process*.

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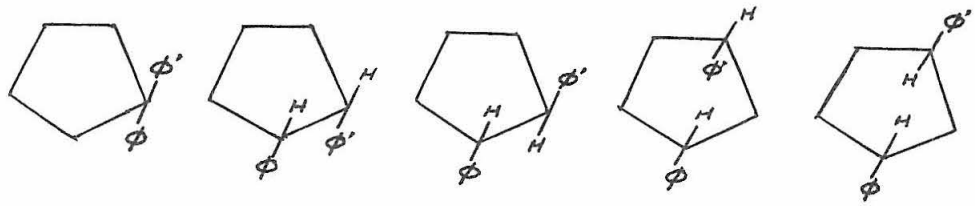
* In this series of compounds, $\delta = \beta^2 \Delta E^{-1}$ should be used.



ϕ ... phenyl ring with no D substitution.
ϕ' ... phenyl ring with different degree of D substitution.

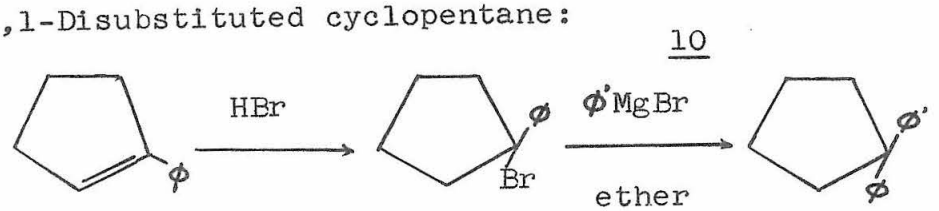
These compounds can be introduced into the rare gas matrix, such as Ne and Ar. The solute to solvent ratio should be kept low enough to avoid any possible intermolecular interaction (9). Then the phosphorescence spectrum can be taken at very low temperature, probably below λ-temperature being necessary for a sharp line spectrum. Whether there is triplet energy transfer or not may be judged by the same method Robinson used (5), namely the comparison of the ratio of the emission intensity from two substituted rings. Whether there is energy shift of the triplet state may be determined by the comparison of the emission spectra with the parent compound, i.e., monosubstituted compounds.

Two advantages can be seen from this system. (i) As pointed out by Robinson, the interaction element is strongly dependent on the distance and the orientation of

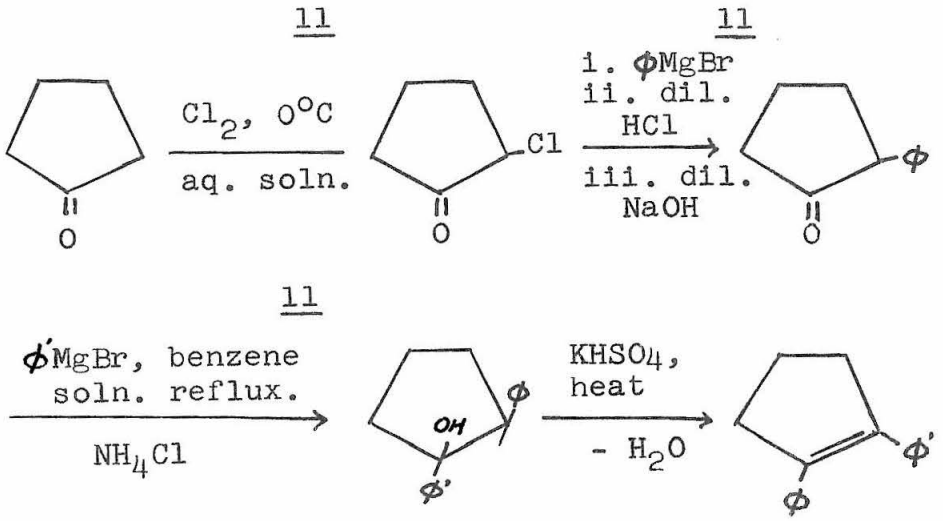
the benzene π-orbitals. Since the conformations of chromophores in these molecules are obvious due to the steric inhibition (two phenyl rings will prefer to be perpendicular to the plane of the cyclopentane ring), a study of the variation with these factors is possible. Comparison of β's of different positional isomers but with the same geometrical structures an estimation of β variation with distance may be made. Same comparison can be done with geometrical isomers for the orientation factor. (ii) It is possible to put some substituent on phenyl rings to give a small perturbation on the ring energy. Presumably, a small substituent will not change the conformation appreciably. (Molecular model has been tried. It shows that a methyl substitution on carbon 2, 3 or 4 on the phenyl ring does not cause great steric effect.) Thus the interaction element may be made for substituted phenyl without worrying about the distortion of crystal structure.

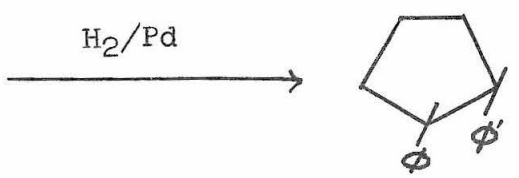
Suggested synthetic routes for diphenylcyclopentane.

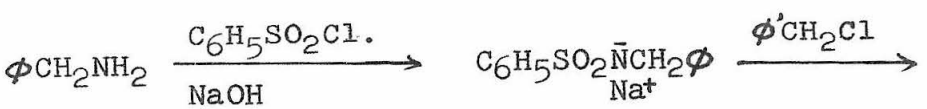
I. 1,1-Disubstituted cyclopentane:

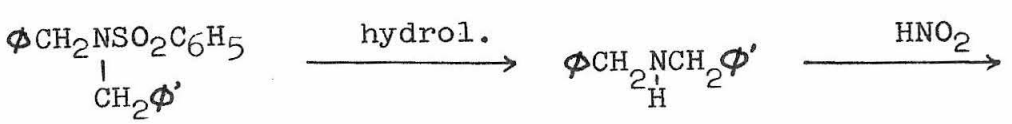


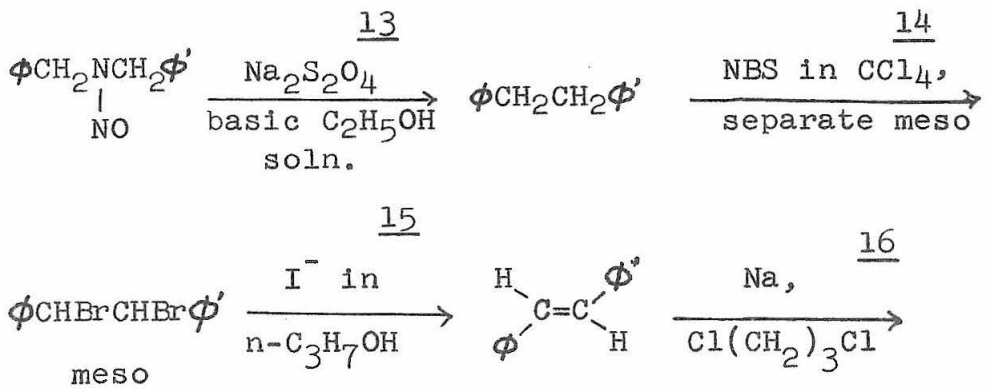
II. 1,2-Disubstituted cyclopentane:

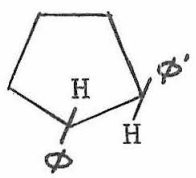




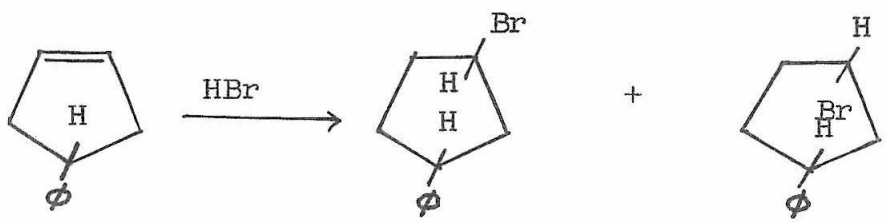


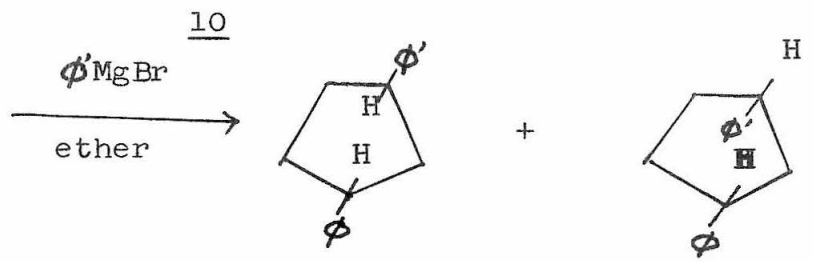






III. 1,3-Disubstituted cyclopentane:





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PROPOSITION V

Azines are proposed as the source of "aryne" and the studies of "aryne" thus produced at low temperature can give the structural information of this intermediate.

Strong evidences had been found that "aryne" plays a very important role in the nucleophilic substitution reactions. For instance, from the study of the amination of aromatic halide using C^{14}-trace, kinetic hydrogen isotopic effects and substituent effects in the orientation in the amination of substituted halobenzenes (1-3).

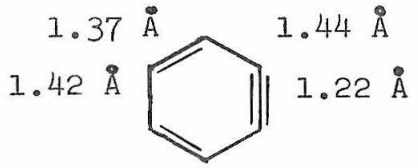
The direct evidences for the existence of benzyne have been reported. I. P. Fisher (4) claimed that a signal of mass 76 has been detected in the thermal decomposition of 1,2-diiodobenzene in a reactor coupled to a mass spectrometer. They assigned it as benzyne.

In the study of the flash photolysis of diazotized anthranilic acid, a spectrum of the intermediate is thought due to benzyne (5, 6).

The structure of "aryne" has been a subject discussed for years. Roberts et al (2), from simple atomic orbital diagram of benzyne, concluded that the molecule might have

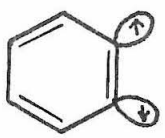
essentially the same resonance energy as benzene if the regular hexagonal structure is still assumed. Furthermore, he pointed out that the strain energy for this structure is comparable with cyclopropene. It is widely accepted that the aromatic character of cyclic system in the aryne intermediate is undisturbed (7).

Further investigations has been done. C. A. Coulson (8) used a simplified calculation pointing out the bond lengths as shown.

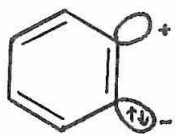


H. E. Simmons (9) made a thorough discussion about the structure of the benzyne. His result excluded the possible "diradical" character of the "triplet bond" of benzyne, which is also inferred from that benzyne does not show characteristic radical reactions. Furthermore, he pointed out that among the three resonance forms, which has been used for a long time, the energy of I will be lower than II or III by about 4.8 eV. (See next page) He concluded that a "new" bond is formed in the benzyne, which is different from a π bond in usual sense. The positive

overlapping receives contributions from both σ and π electron distributions.



I



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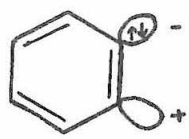
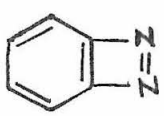
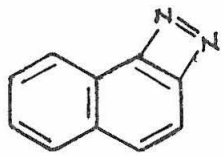
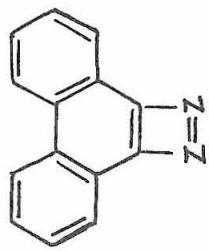


III

However, up to now, there is no "aryne" isolated. It is proposed that the photo-decomposition of the azines shown below in the crystalline rare gas matrix under low temperature may isolate arynes.







By considering the structural similarity of these compounds with analogous hydrocarbons, they may have high vapour pressure too. Therefore, they may be transferred together with krypton or xenon into a sample tube immersed in liquid nitrogen in the system which is evacuated previously. Irradiation with UV of proper wavelength may take off the nitrogen molecules from these azines (14, 15) and give the aryne trapped in the matrix. Under the

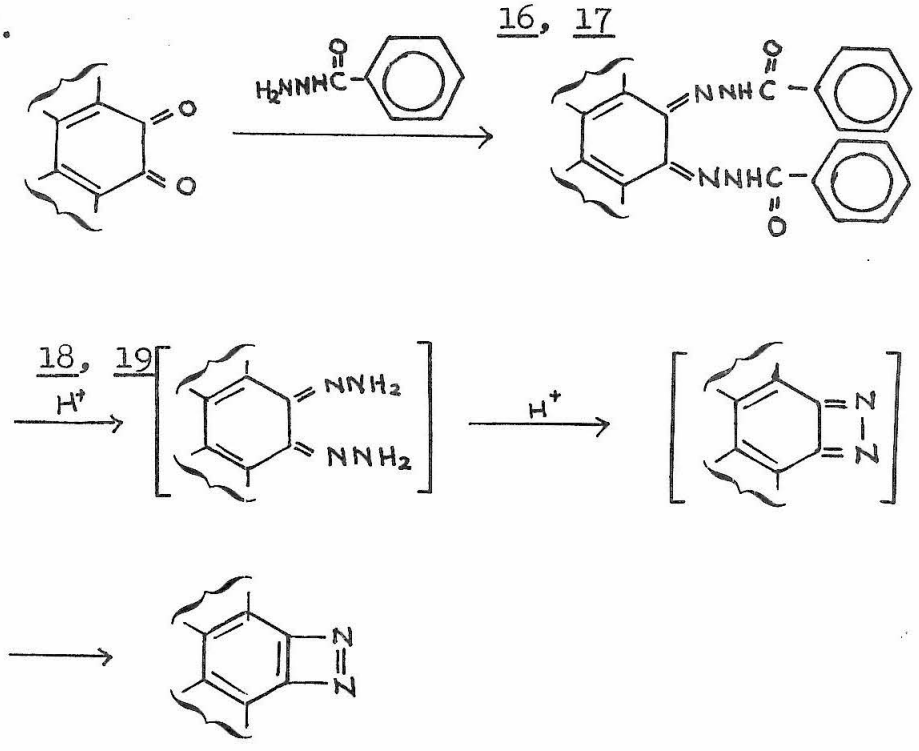
liquid nitrogen temperature and within the noble gas matrix, these arynes are likely to be stable enough for the detection, especially 9,10-phenanthryne, which is the most stable aryne among these three. UV spectra may be taken with the sample still in the liquid nitrogen temperature. The spectrum may be compared with that obtained in the photolysis.

Furthermore, IR study may offer some structural parameters for the determination of the "aryne" structure.

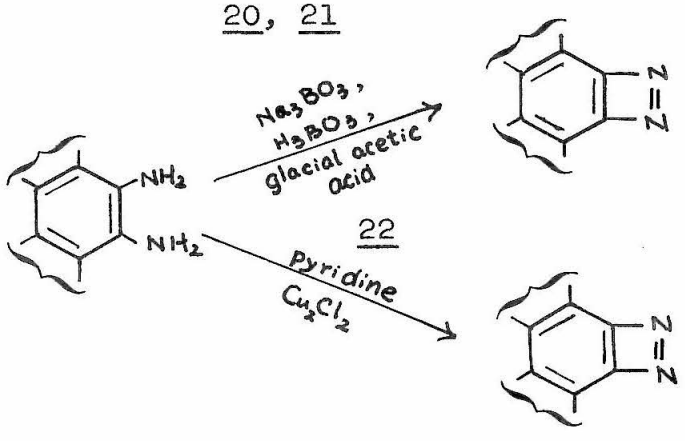
Finally, this may be a better source of aryne. As Lester Friedman (10) pointed out that most methods (fragmentation of suitable ortho-disubstituted benzenes) were found of limited use because of the cumbersome experimental techniques and low yields of the desired products. So far, the thermal decomposition of the diazotized anthranilic acid is thought to be the best (11, 12). R. Knorr indicated the defect of this source because of the solubility of diazotized anthranilic acid. Since most azines are soluble in organic solvents. This may be a better source of aryne. Moreover, the triplet of the aryne is possible to be produced by the sensitization technique.

Suggested sybthetic routes:

I.



II.



In the method II, people obtained intermolecular azines by adding the oxidant into the diamino compound. The reverse step may lead to the intramolecular azines.

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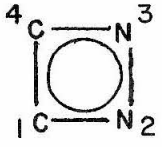
ADDENDUM OF PROPOSITION V

I. The "azine" compounds proposed should be stable and therefore can be synthesized:

HMO calculation of the "parent" compound, 1,2-diazocyclobutadiene, is done.



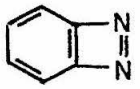
The Coulombic integral of the heteroatom, nitrogen, is expressed in terms of carbon atom's Coulombic integral and resonance integral, i.e., $\alpha_N = \alpha_C + 2\beta(1, 2)$. The resonance integral is assumed the same, β, between two neighboring atoms for C-C, C-N and N-N bonds (1, 2). The secular determinant is then as follows:

$$\begin{vmatrix} \alpha - E & \beta & 0 & \beta \\ \beta & \alpha + 2\beta - E & \beta & 0 \\ 0 & \beta & \alpha + 2\beta - E & \beta \\ \beta & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

or

$$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x+2 & 1 & 0 \\ 0 & 1 & x+2 & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0$$

where $x = (\alpha - E)/\beta$. Four roots of this equation are - 3.414, - 1.414, - 0.586 and 1.414, corresponding to four energy levels with their energies equal to $\alpha + 3.414\,\beta$, $\alpha + 1.414\,\beta$, $\alpha + 0.586\,\beta$ and $\alpha - 1.414\,\beta$. Unlike its hydrocarbon analogue, cyclobutadiene, there is no degenerate energy levels. This is, of course, the result of the reduced symmetry from D_{2h} of cyclobutadiene to C_{2v} of 1,2-diazocyclobutadiene. Consequently, the ground state is not likely to be a triplet state. Its instability cannot be attributed to the unstable triplet ground state as in the cyclobutadiene case (3). However, just like cyclobutadiene, 1,2-diazocyclobutadiene has zero delocalization (resonance) energy. Therefore, the synthesis of the "parent" compound is very improbable.

However, just like in the cyclobutadiene case, compounds derived from fusing 1.2-diazocyclobutadiene to other aromatic systems, i.e., the compounds suggested in this proposition, should be stable. For instance, J. D. Roberts et al predicted that 1,2-benzocyclobutadiene, the hydrocarbon analogue of  (name it as 1,2-diazo-3,4-benzocyclobutadiene,

DBC), has a singlet ground state with substantial delocalization energy, 2.38 β (3).

The HMO computation of DBC is too complicated to do by hand. However, it is very likely the delocalization energy, energy levels and other natures of this compound will not be much differnt from its hydrocarbon analogure. This conclusion is inferred by comparing the HMO calculation of pyridazine with that of benzene. They have comparable delocalization energies and the bond orders of N-N, C-N and C-C in pyridazine are only slightly different from those of C-C in benzene (2). This is due to that in the larger aromatic systems, the perturbation caused by two azo substitutions is not as large as in the cyclobutadiene case.

Furthermore, the strain energy of the four-membered ring should be low, since the more strained 1,2-diazacyclopropenes are known with decomposition temperatures as high as around 220° C (4)*.

Therefore, the "azine" should be stable enough to be synthesized. The intermolecular azines have been synthesized by the ways shown in this proposition. By adding ortho-diamino-hydrocarbons into the oxidant under proper conditions, such as low temperature, vigorous stirring, low concentration of the diamino-compounds and using viscous solvent, to reduce the

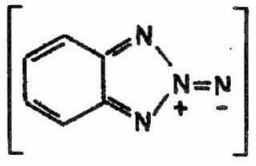
* 1,2-Diazocyclobuene derivatives are also reported (13).

chance for the intermolecular reaction, the intramolecular azines are likely to be produced.

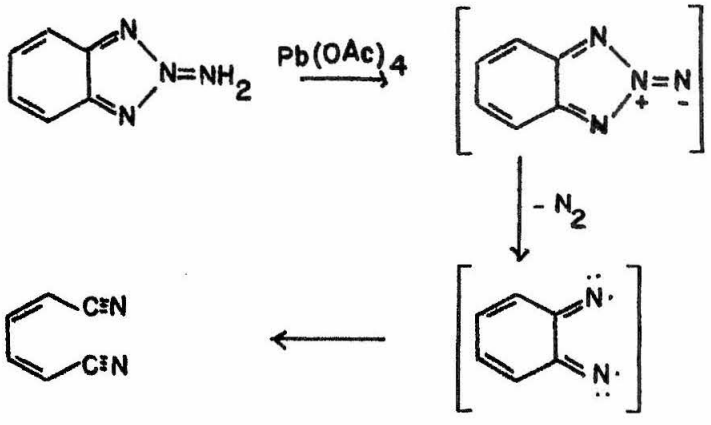
II. Photo-decomposition of the "azines" should generate benzyne:

J. H. Hall et al reported the thermal decomposition of o-diazidobenzene to 1,6-(2,4-hexadiene)-dinitrile (5, 6).

They demonstrated that the intermediate in this reaction is



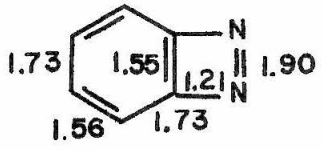
The conclusion is reached by the following reaction (6, 7),



The dinitrene is generated by the evolution of one nitrogen molecule from this first intermediate and it gives the final product by the ring cleavage. They also suggested the other alternative, the evolution of the nitrogen molecule and the ring cleavage happen simultaneously.

However, the ring cleavage is favored at the high temperature they used. This may make other reaction routes of the energetic dinitrene, for instance, the formation of "azine", unfavorable. Consequently, no benzyne addition products can be observed (5, 6).

Using the same reasoning as Part I, the bond orders of DBC should be close to those of its hydrocarbon analogue (3).



Considering the bond orders, the cleavages of two C-N bonds of less double bond characteristics should be energetically favored over the cleavage of the ring to give the open chain compound. Furthermore, comparing the final products of the two alternatives, benzyne, which has been considered to have the same resonance energy as benzene*, and nitrogen molecule

*The reactivity of benzyne is due to the very strained olefin-like bond (9).

should be favored because of their high heats of the formation[1].

Therefore, the photodecomposition of "azine" is more likely to give benzyne.

III. Final remark.

To my surprise, the photodecomposition of o-diazidobenzene has not yet been reported[2].

However, the photodecomposition of p-diazidobenzene in EPA glass at 77° K has been reported (11, 12). The decomposition undergoes by losing nitrogen molecules in steps (11).

diazide $\xrightarrow{h\nu}$ azidonitrene $\xrightarrow{h\nu}$ dinetrene.

The dinitrene is found to be stable at this condition. At room temperature, the thermal decompostion of p-diazidobenzene does not give nitrile but polyazobenzene (6).

It will be interesting to observe the photodecomposition of o-diazidobenzene in the EPA glass and at liquid nitrogen temperature. Three reaction routes are possible, as follows:

1. Like the thermal decomposition, giving dinitrile.
2. Like p-diazidobenzene, giving dinitrene.
3. Forming the azine DBC, whose absorption spectrum should be

[1] The heat of formation of benzyne is estimated to be 124 kcal per mole (10).

[2] I have checked Chemical Abstract up to Nov. 24, 1969.

different from that of diazidobenzene and therefore proper filter system must be used.

These possible products can be distinguished from each other. Only dinitrene shows EPR signal (11). IR spectroscopy can be employed to distinguish the dinitrile from the azine. Dinitrile should show the characteristic -C≡N band, ~2300 cm^{-1} (14) while azine should show N=N band, ~1550 cm^{-1} (13, 14)*.

* 1,2-Diazocyclobutene derivatives show N=N band around this wavenumber (13).

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